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ON THE DECOMPOSITION OF DIAZO-COMPOUNDS.

VIII.—A STUDY OF THE ACTION OF THE SALTS OF DIAZO-BENZENE ON METHYL AND ETHYL ALCOHOLS UNDER DIFFERENT CONDITIONS.[1]

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The work, the results of which are recorded in the following pages, was undertaken at the suggestion of Professor Remsen, and carried on under his guidance, and had for its object the careful study of the decomposition of the salts of diazo-benzene by methyl alcohol alone and by methyl and ethyl alcohols in the presence of certain other substances.

Action of Diazo-benzene Nitrate on Methyl Alcohol.

I.—Portions of the diazo-compound, varying from 30 to 80 grams, were placed in a one-litre flask, and anhydrous methyl alcohol added in the proportion of 5 cc. of the former to 1 gram of the diazo-salt, connected with an inverted condenser and slowly heated. A slow decomposition began at the room temperature. This grew more rapid as the temperature was raised, until at 30°–35° C. there was a rapid decomposition accompanied by a copious evolution of nitrogen gas and a gradual rise in temperature to the boiling-point of the alcohol without the further application of heat. 222 grams of the diazo salt and methyl

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alcohol were thus decomposed and the residues united. During all of these decompositions (six in number) no odor of aldehyde was perceptible, nor had the residues the odor of aldehyde. In the case of two or three the escaping gas was passed through either water or methyl alcohol, and the liquid examined for aldehyde by treating with an ammoniacal solution of silver nitrate, but there was no evidence of the presence of aldehyde. The united residues, which were strongly acid and had the odor of anisol, were poured into a one-litre flask and the alcohol and volatile products distilled off. The methyl alcohol thus obtained, which was slightly yellow, due to the presence of anisol, was poured into two-litre flasks, and six volumes of a saturated solution of sodium chloride added. There rapidly rose into the neck of the flask an amber-colored oil, which was removed by means of a pipette. The methyl alcohol was then distilled off the salt-solution, and the first three portions of 20 cc. each were separately treated with six volumes of salt-solution and allowed to stand. There separated from the first two portions a small quantity of an oil having the same odor and appearance as that obtained in the first instance, to which it was added. The tarry contents of the flask from which the methyl alcohol had been distilled were made alkaline with caustic soda and distilled in steam. There was thus obtained a considerable quantity of oil resembling that obtained in the preceding cases. These portions were united, dried over fused calcium chloride, and subjected to fractional distillation. Almost the entire product passed over at 148°–153° C., and proved to be anisol or methoxy-benzene. No trace of benzene was found.

The contents of the flask which had been distilled in steam to remove the anisol were acidified with sulphuric acid and further distilled in steam. A yellow solid slowly collected in the condenser and receiver, while the water had a deep yellow color. This operation was continued until the solid ceased to collect, and further, until the liquid which came over was almost colorless. The liquid was filtered from the solid, made alkaline with caustic soda, and evaporated to a small bulk. Upon acidifying with hydrochloric acid, a whitish-yellow substance was precipitated which, upon further examination, proved to be the same as the solid obtained in the first instance. These were united and subjected to careful crystallization, first from hot water and then from alcohol. In each case the substance was obtained in the

form of whitish-yellow plates which melted at 114° C. (Zincke thermometer) and otherwise had the properties of 2:4-dinitrophenol. The liquid remaining in the flask through which steam had been passed was separated from the tarry substance which had been formed in the decomposition, was boiled with animal charcoal and evaporated down in stages. No definite substance was obtained from the tarry residue.

From the 222 grams of diazo-benzene nitrate 58.2 grams of anisol (40 per cent.) and 20 grams of 2 : 4-dinitrophenol were obtained.

Plainly the principal reaction that has taken place in this case is that represented by the following equation:

$$C_6H_5.N_2.NO_3 + CH_3OH = C_6H_5OCH_3 + N_2 + HNO_3.$$

Remsen and Orndorff have shown[1] that with ethyl alcohol this same diazo-compound gives principally the ethoxy-derivative together with a small quantity of benzene. No benzene is obtained when methyl alcohol is used. This is quite in accordance with other facts established in the course of this series of investigations, and points to the conclusion that the simpler the alcohol the greater the tendency to the alkoxy-reaction.

As regards the dinitrophenol, it was thought improbable that the comparatively large quantity of this substance obtained was due to the presence of water in the alcohol, for this had been distilled from lime over which it had stood for some days. The presence of water would probably account for a small portion, but not for the entire 20 grams of the substance. It was thought more probable that ortho-nitrophenol may have been first formed by a molecular rearrangement of the diazo-compound, as was found to be true by Remsen and Orndorff in the case of the action of diazo-benzene nitrate on ethyl alcohol,[2] and the mono-nitrophenol thus formed further nitrated to the dinitrophenol (*a*) either by the action of the nascent nitric acid during the decomposition, (*b*) or by standing in contact with the free nitric acid, (*c*) or while heating to distill off the alcohol and anisol. If ortho-nitrophenol is first formed and not further nitrated by the nascent nitric acid, then by making alkaline as soon as the decomposition had ceased only ortho-nitrophenol should be found. In order to throw light upon this point the following experiment was performed.

[1] This Journal **9**, 387. [2] *Ibid.* **9**, 389.

II.—Forty-two grams of diazo-benzene nitrate and methyl alcohol (off lime) were decomposed under conditions similar to those in the preceding case. The contents of the flask were made alkaline with caustic soda solution as soon as the decomposition had ceased. The alcohol was distilled off and the anisol obtained by pouring into a saturated solution of sodium chloride. The tarry residue was distilled in steam to remove the anisol, then made acid with sulphuric acid and further distilled in steam. A yellow solid rapidly collected in the condenser, which crystallized from hot alcohol in long yellow needles, melting at 45° C., and possessing the general properties of ortho-nitrophenol. The liquid remaining in the flask was separated from the tarry substance, boiled with animal charcoal, evaporated to a small bulk, filtered, and about an equal volume of strong hydrochloric acid added. Upon standing, long, almost colorless needles crystallized out, which upon further crystallization from hot water were colorless, melted at 115° C., and otherwise had the properties of para-nitrophenol.

Products: Anisol 12 grams, or 42.5 per cent.
Ortho-nitrophenol 2 grams, or 5.7 per cent.
Para-nitrophenol 0.4–0.5 gram, or 1.2 per cent.

This indicates that mono-nitrophenols were first formed, and then nitrated to the dinitrophenol, either while standing in contact with the free nitric acid or when the alcohol is distilled off. The ortho-compound was doubtless formed by the molecular rearrangement of the diazo-benzene nitrate with the loss of nitrogen, as before mentioned, but the presence of the small amount of the para-compound was probably due to the presence of a small quantity of water in the alcohol. Remsen and Orndorff found that on heating diazo-benzene nitrate in a neutral liquid (toluene) 24 per cent. of it was converted into ortho-nitrophenol, as expressed by the following equation: $C_6H_5N_2NO_3 = C_6H_4 < \begin{matrix} OH \\ NO_2 \end{matrix} + N_2$, while "not a trace of the para-compound was found."[1] This in itself does not prove that no para-nitrophenol will be formed when the diazo-salt is decomposed with alcohol, for in the one case the decomposition is effected in the presence of a liquid supposed to be neutral, in the other case with a liquid which is known to be capable of reacting with it.

[1] This Journal **9**, 391.

III.—The preceding experiment was now repeated, using absolute methyl alcohol. This was prepared by treating the alcohol which had been distilled from lime, with anhydrous copper sulphate, and letting them stand together for several days. The alcohol was then poured off and redistilled. The only products obtained were anisol and ortho-nitrophenol. A careful examination was made for the para-compound by separating from the tarry mass the liquid remaining in the flask through which steam had been passed to remove the ortho-compound, and then evaporating it down in stages, each time adding strong hydrochloric acid and letting cool. No organic matter crystallized out. The liquid was then evaporated to dryness and the residue of inorganic salts treated with hot alcohol. The alcohol was colored slightly yellow, but no para-nitrophenol was obtained from it. This experiment was repeated, but in this case also no para-nitrophenol was found. Hence it was concluded that when diazo-benzene nitrate is decomposed with absolute methyl alcohol the products of the reaction are anisol and ortho-nitrophenol.

IV.—In order to determine whether the nitration of the ortho-nitrophenol to the dinitro-compound took place on standing in contact with the free nitric acid, or when heating to distill off the alcohol, 42 grams of the diazo-salt were decomposed with methyl alcohol, allowed to stand over night, and then made alkaline with caustic soda solution.

Products: Anisol 13 grams, or 48 per cent.
Ortho-nitrophenol 1.7 grams, or 5 per cent.
Dinitrophenol 1 gram, or 2.2 per cent.

Probably more of the mono-nitrophenol would be converted into the dinitro-compound by allowing the liquid to stand longer before neutralizing the nitric acid.

The fact that only ortho-nitrophenol is formed when diazo-benzene nitrate is decomposed with absolute methyl alcohol (III) is evidence that no para-compound is formed by the molecular rearrangement, but it is only negative proof that the para-compound obtained in case II was due to the presence of a small quantity of water in the alcohol. If, however, this be the case, then dilute methyl alcohol should give an increased percentage of both the ortho- and para-nitrophenols, for both would be formed by the action of the free nitric acid on phenol.

V.—Fifty grams of the diazo-salt were decomposed with 250 cc. of methyl alcohol diluted with 30 per cent. of water, at the room temperature, and the liquid made alkaline with caustic soda solution as soon as the action had ceased. The diazo-compound dissolved to a wine-colored liquid. The decomposition began without the application of heat and was allowed to decompose spontaneously.

Products: Anisol 4.5 grams, or 14 per cent.

Ortho-nitrophenol 5 grams, or 12 per cent.
Para-nitrophenol 2.4 grams, 6 per cent. } 18 per cent.

For comparison I repeat the results obtained in case II with alcohol off lime:

Anisol 42 per cent.

Ortho-nitrophenol 5.7 per cent.
Para-nitrophenol 1.2 per cent. } 6.9 per cent.

With absolute alcohol the products obtained were anisol and ortho-nitrophenol.

It will be noticed that there is a large increase in the percentage of both the ortho- and para-nitrophenols in case V over that in case II, due to the presence of a larger amount of water in the former. But the decrease in the percentage of the anisol (28 per cent.) is too large to be accounted for by the assumption that the water present in case V uses up the diazo-salt to form phenol, of which action the increased percentage of the nitrophenols (11 per cent.) is a measure. This discrepancy, it was thought, might be due to the difference in temperature at which the two decompositions were effected, for it has been shown by Remsen and Dashiell that increased temperature and pressure increase the alkoxy reaction.[1]

VI.—In order to make the results in the two cases strictly comparable, 71 grams of the diazo-salt were decomposed with methyl alcohol at the room temperature without dilution, and the contents of the flask made alkaline as soon as the decomposition had ceased. The products, separated as in the preceding cases, were:

Anisol 27 per cent.

Ortho-nitrophenol 5.6 per cent.

Upon comparing these results with those obtained in the preceding experiment it will be seen that the increase in the total

[1] This Journal 15, 125-6.

percentage of the nitrophenols (12.4 per cent.) due to the presence of water, and the decrease in the percentage of anisol (13 per cent.) due to the using up of the diazo-salt by the water to form phenol and then nitrophenol, mutually account for each other. The presence of the water in case V also accounts for the formation of the para-nitrophenol, and for the increased percentage of the ortho-compound, for both are produced by the nitration of phenol.

Upon comparing the results obtained in cases II and VI there will be noticed a considerable decrease in the percentage of anisol formed at the lower temperature. This is of special interest, because here a high temperature apart from pressure appears to favor the alkoxy reaction. Remsen and Dashiell effected the decomposition of a diazo-compound with alcohol in a suitable flask, under increased pressure and temperature, but were unable to determine which was the primary cause in influencing the alkoxy reaction, whether the high temperature conditioned by the increased pressure, or the increased pressure due to an elevated temperature. In order to throw light upon this point they brought together a diazo-compound and alcohol under varying pressures without a corresponding change of temperature. But the decomposition would not take place except at the temperature of the boiling-point of the alcohol at that pressure.[1]

While the results obtained in cases II and VI indicate that the elevated temperature favors the alkoxy reaction, they do not indicate that a lower temperature favors the hydrogen reaction. To test this point a diazo-compound and alcohol must be selected which give both the hydrogen and alkoxy reactions. Diazo-benzene nitrate and ethyl alcohol do this, and hence the following experiment was performed.

VII.—150 grams of diazo-benzene nitrate and ethyl alcohol distilled from lime were decomposed in two lots, *A* and *B*, at the room temperature. The action was slow, accompanied by a slight elevation of temperature and a gradual reddening and darkening of the alcohol. From two to three days were required for the completion of the decomposition.

A. 119 grams of the diazo-salt and about 500 cc. of ethyl alcohol were allowed to stand together at the room temperature

[1] This Journal **15**, 125.

until decomposition had ceased. The volatile products were distilled off and the residue then made alkaline with caustic soda solution, and distilled in steam to remove the phenetol. This distillate was added to the alcoholic distillate and set aside. Upon acidifying and further distilling in steam, 2 : 4-dinitrophenol was obtained, the quantity being less than was obtained in the corresponding case, when methyl alcohol distilled from lime was used.

B. 35 grams of the diazo-salt were decomposed with absolute ethyl alcohol at the room temperature, and made alkaline as soon as the decomposition had ceased. There were obtained 3 grams of ortho-nitrophenol, but no para-compound. These results confirm the conclusions drawn in the corresponding cases with diazo-benzene nitrate and methyl alcohol.

The alcoholic distillates from the two decompositions were united and poured into six volumes of a saturated solution of sodium chloride. A rather dark-colored liquid, having the odor of aldehyde, rapidly rose. This was collected, dried over fused calcium chloride and subjected to careful fractional distillation. From the 30 grams of the dried liquid there were obtained 6.4 grams of phenetol. But the other constituents could not be separated by this means. Strong sulphuric acid was added, the liquid darkened, and upon gentle heating there began a copious evolution of ordinary aldehyde. When this had ceased strong nitric acid was added, and nitrobenzene was obtained. Phenetol, nitrophenols, diphenyl, paraldehyde, and benzene were thus obtained. The quantity of diphenyl formed was very small, probably not over 0.5 gram. It was doubtless formed by the union of the two phenyl residues in the nascent state, as it is found in many cases where benzene is being formed—*e. g.* from benzoic acid and lime.

The ratio of the phenetol to the benzene was not determined in this case, as a portion of the latter was doubtless acted upon by the sulphuric acid, and a part of it carried off mechanically by the rapid escape of the aldehyde. So about the same quantity of the diazo-salt as was used in the preceding case was decomposed with alcohol, and the decomposition-flask kept in a bath of cold water to prevent a rise in temperature during the decomposition. The products were obtained as in the preceding case, and the phenetol separated as before by fractional distillation. The mixture of paraldehyde and benzene was poured into a

small flask connected with an inverted condenser, strong nitric acid was added and the flask heated, when there began a copious evolution of aldehyde which continued until all of the paraldehyde was broken down. The remaining liquid was separated from the acid and distilled. 12 grams of the liquid distilled over at 78°–85° C., the few drops remaining were nitrobenzene. The distillate, which had a slight odor of aldehyde, was treated with a mixture of concentrated nitric and sulphuric acids. There were thus obtained 18 grams of nitrobenzene, equal to 10 grams of benzene. From the 27.5 grams of the mixture there were obtained phenetol 2 grams, benzene 12 grams, and paraldehyde 13.5 grams. Here, it will be seen, the principal product of the reaction was benzene, while in the case of the decomposition of the same diazo-salt and alcohol at a higher temperature (above 50°–60° C.) Remsen and Orndorff got mainly the alkoxy product. For comparisons I give their results:[1]

Phenetol, 22 per cent.

Benzene, 4 per cent.

This shows that, in this case at least, the temperature apart from pressure influences the character of the reaction, the higher temperature favoring the alkoxy reaction, the lower temperature the hydrogen reaction.

Effect of the Presence of Water upon the Diazo-Alcohol Reaction.

In the case of the methyl alcohol and diazo-benzene nitrate, it will be seen, upon comparing experiments V and VI, that the presence of 30 per cent. of water had no effect upon the character of the reaction except to decrease the percentage of the anisol, and proportionally to increase that of the nitrophenols. It was thought desirable to study the action of dilute ethyl alcohol on diazo-benzene nitrate.

A. 50 grams of the diazo-salt and 200 cc. of ethyl alcohol diluted with 30 per cent. of water were decomposed at the room temperature, and the liquid made alkaline as soon as the action had ceased. The products, obtained as in the preceding case, were:

Ortho-nitrophenol 5 grams, or 12 per cent.

Dinitrophenol 2.2 grams, or 5 per cent.

Phenetol 4 grams, or 11 per cent.

[1] This Journal **9**, 389.

and 2 grams of a liquid which distilled over between 75° and 85° C. and had the odor of aldehyde. This contained paraldehyde, for upon adding strong sulphuric acid and heating an evolution of aldehyde took place. Nitric acid was then added to the remaining liquid and this heated for some time. Upon pouring the whole into a small beaker of water, a few small globules, apparently of nitrobenzene, collected. At any rate the principal product was the alkoxy compound. This experiment was repeated, using less dilute alcohol.

B. 35 grams of the diazo-salt were decomposed with ethyl alcohol diluted with 10 per cent. of water. The flask was kept as near the room temperature as possible, by placing the decomposition flask in a bath of water. The products were collected as in the preceding case. From the 8 grams of the mixture there were obtained 5 grams of phenetol and 2 grams of a low-boiling liquid, which upon the addition of strong nitric acid and heating, was almost completely converted into aldehyde. In this case 0.5 gram of diphenyl was formed. No examination was made for nitrophenols.

By comparing these results with those obtained in the preceding case it will be seen that the presence of a small percentage of water favors the formation of the ethoxy product.

Action of Diazo-benzene Nitrate on Sodium Methylate.

In the preceding decompositions the yields of the alkoxy products were rather small, in each case a large amount of tarry substance and in some instances not an inconsiderable quantity of nitrophenols being formed. It was thought probable that if something were present during the reaction to combine with the acid, the formation of the nitrophenols might be prevented. Hence the action of sodium methylate on diazo-benzene nitrate was tried, in the expectation that the following reaction would take place: $C_6H_5N_2NO_3 + NaOCH_3 = C_6H_5OCH_3 + NaNO_3 + N_2$.

A saturated solution of sodium methylate in methyl alcohol was prepared by dropping small pieces of pure metallic sodium into absolute methyl alcohol in a flask kept cool in an ice-water bath until the sodium ceased to react further with the alcohol. To this 87 grams of diazo-benzene nitrate were added little by little, stirring meanwhile. The flask was kept in the ice-water so that the

temperature did not rise above 20°–25° C. The action took place energetically with the evolution of nitrogen gas and a rise in temperature. The diazo-body was partly changed into a yellowish gummy mass, while the liquid gradually darkened. A peculiar penetrating odor was observed during the decomposition. This was thought to be due to the formation of formic aldehyde. Some of the escaping gas was passed through water and some through methyl alcohol, in the hope of absorbing the aldehyde if present. These liquids were then tested for aldehyde by treating with an ammoniacal solution of silver nitrate, but there was no reduction. This test was made in the case of several of the decompositions, and with the same results.

The methyl alcohol and volatile products were then distilled off and poured into about five volumes of water. There rose a considerable quantity of clear liquid having the odor of benzene. This was dried over fused calcium chloride and distilled. The whole passed over at 78°–83° C. The liquid solidified at 1°–2° C., and, with strong nitric and sulphuric acids, gave nitrobenzene. Hence there can be no doubt that the substance was benzene. The liquid from which the benzene had been obtained was then saturated with sodium chloride, but no anisol separated out.

Water was then added to the contents of the flask from which the alcohol and benzene had been distilled, and this distilled in steam. The first 100 cc. of the distillate were treated with six volumes of a saturated solution of sodium chloride, but nothing was thus obtained. A red solid rapidly collected in the condenser and receiver. The distillation in steam was continued until the solid ceased to collect, then the contents of the flask were acidified with sulphuric acid and further distilled in steam, but nothing was obtained. The liquid remaining in the flask was separated from the tarry substance and evaporated down in stages. The only compounds obtained were sodium nitrate and sodium sulphate. The red solid was crystallized several times from hot alcohol, from which it was obtained in the form of small white pearly plates, which melted at 67.9° C. (uncorrected), and otherwise had the properties of diphenyl. The products of the decomposition were:

Benzene 20 grams, or 50 per cent.

Diphenyl, about 7 grams, or 15 per cent.

In order to account for the formation of the diphenyl the following reaction may be supposed to take place:

$$\begin{matrix} C_6H_3N_2NO_3 \\ C_6H_3N_2NO_3 \end{matrix} + \begin{matrix} NaOCH_3 \\ NaOCH_3 \end{matrix} = \begin{matrix} C_6H_5 \\ | \\ C_6H_5 \end{matrix} + 2N_2 + 2NaNO_3 + 2OCH_2.$$

The two alkoxy residues would probably unite to form methyl alcohol and formic aldehyde.

In regard to the formation of the benzene there are two ways in which it may be accounted for: (*a*) by supposing the action between the diazo-salt and the sodium methylate to give an intermediate product, and this to break down into formic aldehyde, nitrogen and benzene, according to the following equation: $C_6H_3N_2NO_3 + NaOCH_3 = NaNO_3 + C_6H_5N_2OCH_2 = C_6H_6 + N_2 + CH_2O$; or, (*b*) by supposing a reaction to take place between the diazo-compound and the alcohol in which the sodium methylate was dissolved, giving the well-known hydrogen reaction. The latter supposition seems hardly probable, since there was a large excess of the sodium methylate present, and since methyl alcohol, at the same temperature at which this decomposition was effected, gave only the methoxy product. It may be, however, that the sodium methylate simply acts as an alkali, neutralizing the acid of the nitrate and setting free the diazo-compound. If this view be correct, then the presence of any alkali, or any other substance that would combine with the acid, ought to lead to the hydrogen reaction. To test this the next experiments were tried.

Action of Diazo-benzene Nitrate on Methyl Alcohol in the Presence of Alkalis and of Calcite.

A. 70 grams of the diazo-salt were decomposed with absolute methyl alcohol in the presence of an excess of pure sodium hydroxide. The diazo-compound was slowly added under constant stirring, the temperature being kept below 30° C. by immersing the vessel in a bath of ice-water. The action took place with considerable energy. The general phenomena were the same as in the preceding case. The products obtained, as in the preceding case, were:

Benzene 7 grams, or 22 per cent.

Diphenyl (crude), 8–10 per cent.

B. 60 grams of the diazo-compound and absolute methyl alcohol were decomposed at a temperature below 30° C. in the presence of

an excess of anhydrous sodium carbonate. The action was less energetic than in the two preceding cases.

Products: Benzene 3.1 grams, or 10 per cent.

Diphenyl (crude) 6 grams, or 21 per cent.

C. 61 grams of the diazo-salt and methyl alcohol were allowed to decompose at the room temperature in the presence of an excess of pure calcite. The general phenomena were the same as when the diazo-compound was allowed to decompose at the room temperature with methyl alcohol alone.

Products: Anisol 11 grams, or 25 per cent.

Ortho-nitrophenol, 0.5 gram, or 1 per cent.

It appears from these experiments that the presence of alkalis leads to the hydrogen reaction, while the presence of calcite has no effect upon the character of the reaction.

Action of Diazo-benzene Nitrate on Sodium Ethylate.

The experiments with sodium methylate and methyl alcohol in the presence of alkalis naturally suggested similar ones with sodium ethylate and ethyl alcohol in the presence of alkalis. A saturated solution of sodium ethylate in ethyl alcohol was prepared in a similar manner to that of the sodium methylate, the experiment carried out under the same conditions and the products separated in the same way. The phenomena were in general the same as those in the experiment with sodium methylate, but the action was far more violent in this case, requiring cautious addition of the diazo-body to prevent an ignition of the alcohol. The alcoholic distillate did not have the odor of aldehyde. From the 47 grams of the diazo-compound there were obtained the following products:

Benzene 4.1 grams, or 19 per cent.

Diphenyl (crude) 5 grams, or 17 per cent.

It will be seen that the products are the same as those obtained with sodium methylate, though the yield of benzene was smaller. Relatively a much larger amount of tarry products was obtained in this case than in that of the sodium methylate.

Action of Diazo-benzene Nitrate on Ethyl Alcohol in the Presence of Alkalis.

The conditions under which these decompositions were made were the same as those of the preceding cases; the phenomena in

general were the same, and the products were collected in the same way.

A. 47 grams of the diazo-salt and ethyl alcohol were decomposed in the presence of an excess of anhydrous sodium hydroxide dissolved in the alcohol.

Products: Benzene 5 grams, or 27 per cent., and diphenyl.

The amount of the diphenyl was not determined, but the yield was smaller than that obtained in the case of the sodium ethylate.

B. 50 grams of the diazo-compound were decomposed with ethyl alcohol in the presence of an excess of anhydrous sodium carbonate. The products obtained in this case were:

Diphenyl 1.7 grams, or 6 per cent.

Benzene, Paraldehyde } 15 grams.

The ratio of the benzene to paraldehyde was not determined, since they could not be separated by fractional distillation. But the lower-boiling portions were heated with a mixture of strong nitric and sulphuric acids and converted into nitrobenzene.

From the results obtained in these experiments it appears that the presence of alkalis in general leads to the hydrogen reaction. But since it has been shown that a low temperature favors the hydrogen reaction, it was thought possible that the low temperature at which these decompositions were effected was the determining factor and not the presence of the alkalis. In order to throw light upon this point the next experiments were tried.

Action of Diazo-benzene Nitrate on Methyl and Ethyl Alcohols in the Presence of an Excess of Sodium Hydroxide at an Elevated Temperature.

Since all of these decompositions in the presence of alkalis gave the same products, it did not matter which was repeated at the elevated temperature. Merely for the sake of convenience the one in the presence of caustic soda was selected.

A. 71 grams of the diazo-compound were decomposed with 400 cc. of absolute ethyl alcohol in the presence of an excess of sodium hydroxide at a temperature of 55°–70° C. This is the temperature at which this same diazo-salt and alcohol alone gave mainly the alkoxy product.[1] The decomposition was effected in a flask

[1] This Journal **9**, 389.

with a very long neck, which was wrapped with a wet towel in order to condense any volatile products which tended to escape. The products obtained were:

Benzene 5.5 grams, or 17.5 per cent.

Diphenyl (crude) 1.1 grams, or 4 per cent.

B. 37 grams of the diazo-compound were decomposed with 200 cc. of methyl alcohol in the presence of an excess of caustic soda at a temperature of 50°–55° C.

Products: Benzene 3.5 grams, or 19 per cent.

Diphenyl (crude) 0.9 gram, or 5.5 per cent.

Relatively more tarry products were formed at the high temperature and correspondingly less benzene and diphenyl, than at the low temperature. Otherwise, it will be seen that the character of the reaction was the same in both cases.

This series of experiments shows that in general the presence of alkalis leads to the hydrogen reaction, but just how, it is impossible to say until more facts bearing upon the question are accumulated. It may be that intermediate products are first formed, as was suggested in the case of sodium methylate. In the presence of alkaline hydroxides, then, diazo-benzene would probably first be formed, and this reacting with the alcohol give the hydrogen reaction, as expressed by the following equations: $C_6H_5.N_2NO_3 + NaOH = NaNO_3 + C_6H_5N_2OH$, and $C_6H_5.N_2.OH + CH_3OH = C_6H_6 + N_2 + H_2O + CH_2O$. But this cannot be claimed for the cases in which the decomposition was effected in the presence of sodium carbonate. Then it appears that, since the general phenomena and the products obtained in all these cases were the same, no intermediate products were formed in any of them, and that the hydrogen reaction is due to some other causes, possibly the prevention of the acidity of the medium by the neutralization of the acid at the moment of liberation. If this view be correct, then the presence of any substance which would combine at once with the acid as soon as set free ought to determine the hydrogen reaction. The study of the decompositions in the presence of zinc-dust, given later on, confirms this view. And, on the other hand, the presence of a considerable quantity of free acid ought to increase the amount of the alkoxy products in those cases where both the hydrogen and alkoxy reactions take place. I am not aware that any experiments of this kind have been tried.

Action of Diazo-benzene Sulphate on Methyl Alcohol.

144 grams of this diazo-compound were decomposed with 350 cc. of methyl alcohol distilled from lime. The application of heat was necessary to start the decomposition, which began at 40°–45° C. and continued spontaneously with a gradual rise in temperature to the boiling-point of the alcohol. The general phenomena of the decomposition were the same as in the case of the action between methyl alcohol and diazo-benzene nitrate. The action was a clean one, only a small quantity of tarry materials being formed.

The alcohol and volatile products were distilled off, and the remaining contents of the flask distilled in steam to remove the anisol. The two distillates were treated with about six volumes of a saturated solution of sodium chloride. The oil which rose was collected, dried over calcium chloride and subjected to fractional distillation. About 0.5–1 cc. of a colorless liquid came over below 100° C. when the thermometer rapidly rose to the boiling-point of the anisol, where almost the entire product distilled over. The low-boiling liquid was very volatile and had the odor of methyl alcohol, which it probably was. I think there can be no doubt that no benzene was present in the anisol. The contents of the flask which had been distilled in steam were neutralized with barium carbonate, filtered and evaporated down in stages, being allowed to cool slowly at each stage. The only thing found was aniline sulphate which had escaped diazotization. From the 144 grams of the diazo-benzene sulphate the only product obtained was 40 grams, or 53 per cent., of anisol.

Action of Diazo-benzene Sulphate on Sodium Methylate and Ethylate.

The reaction in these cases took place only to a slight extent, even upon heating to the boiling-points of the alcohols for an hour or more. Almost the whole of the diazo-body in both cases was changed into a hard, black, tarry mass. The alcohols were distilled off and treated with a saturated solution of sodium chloride. From each a small quantity of a dark-colored liquid rose, but the quantities were too small to determine what the products were. The tarry residues were then distilled in steam. In each case a very small quantity of diphenyl was obtained. These

results were surprising, for the diazo-benzene nitrate and the sodium alcoholates reacted energetically at a low temperature, and gave good yields of benzene and diphenyl.

Action of Diazo-benzene Sulphate on Methyl and Ethyl Alcohol in the Presence of an Excess of Zinc-dust.

The previously described decompositions made in the presence of alkalis suggested similar ones in the presence of finely divided metals. Experiments with finely divided copper and iron were not made with this compound, but iron by hydrogen had no effect upon the reaction between diazo-benzene nitrate and methyl alcohol. When diazo-benzene nitrate and sulphate were separately brought together with methyl or ethyl alcohol and zinc-dust added, an energetic reaction at once took place.

A. 51 grams of diazo-benzene sulphate and methyl alcohol were decomposed in the presence of zinc-dust at a temperature below 30° C. The dry zinc-dust and alcohol were placed together in a flask immersed in a bath of ice-water and the diazo-salt slowly added while the liquid was stirred. The action was a clean one, almost no tarry products being formed. The alcohol and volatile products were distilled off, and treated with a saturated sodium chloride solution. A clear liquid rose, was collected, dried over calcium chloride and distilled. The liquid boiled at about 80° C., solidified at 1°–2° C., and otherwise had the properties of benzene. The residue from which the alcohol and benzene had been distilled was now distilled in steam. The only substance thus obtained was diphenyl.

Products: Benzene 3 grams, or 16 per cent.
Diphenyl 1.4 grams, or 7 per cent.

The products obtained in all of the following decompositions in the presence of zinc-dust were obtained by the method described in this case.

B. 77 grams of diazo-benzene sulphate and ethyl alcohol were decomposed in the presence of an excess of zinc-dust. The action in this case was somewhat less energetic than that in the preceding one.

Products: Diphenyl 0.5 gram.
Paraldehyde 26.5 grams.
Benzene 4.5 grams.

The benzene in the mixture of paraldehyde and benzene was estimated by getting rid of the paraldehyde by boiling the mixture

with strong nitric acid in a flask connected with an inverted condenser, and then converting the liquid remaining in the flask into nitrobenzene. The aldehyde was estimated by difference.

Action of Diazo-benzene Nitrate on Methyl and Ethyl Alcohol in the Presence of an Excess of Zinc-dust.

A. 50 grams of diazo-benzene nitrate and methyl alcohol were decomposed in the presence of zinc-dust at a temperature below 30° C.

Products: Benzene 7 grams, or 30 per cent.
Diphenyl 3 grams, or 13 per cent.

The contents of the flask which had been distilled in steam to remove the diphenyl were filtered from the remaining zinc-dust and the tarry products, evaporated to dryness and treated with hot alcohol in the hope of obtaining trioxymethylene or paraformaldehyde, but none was thus obtained.

B. 56 grams of diazo-benzene nitrate and ethyl alcohol were decomposed in the presence of zinc-dust.

The products obtained were diphenyl, 0.5 gram, and a mixture of paraldehyde and benzene. The ratio of these substances was not determined, but the paraldehyde was broken down into aldehyde, and the remaining liquid converted into nitrobenzene.

It will be seen that the results obtained in this series of decompositions are in every way similar to those obtained by the action of diazo-benzene nitrate on the sodium alcoholates, and on methyl and ethyl alcohol in the presence of alkalis. They tend also to confirm the view previously put forward, that the presence of any substance which will combine with the acid at the moment of liberation leads to the hydrogen reaction. There are, however, strong indications that the action is not between the free acid and the neutralizing agent, but largely between the neutralizing agent and the acid portion of the diazo-salt. For if either of the two diazo-compounds be brought together with methyl or ethyl alcohol in the cold, only a slight reaction takes place, but when an alkali or zinc-dust is added an energetic action at once begins. This view would easily account for the formation of the diphenyl, but not for that of the benzene. The following reaction probably takes place between zinc and diazo-benzene nitrate:

$$\begin{matrix} C_6H_5N_2NO_3 \\ C_6H_5N_2NO_3 \end{matrix} + Zn = Zn(NO_3)_2 + 2N_2 + \begin{matrix} C_6H_5 \\ | \\ C_6H_5 \end{matrix}.$$

It therefore seems not improbable that there are two distinct reactions which take place: (*a*) one between the neutralizing agent and the acid portion of the diazo-compound leading to the formation of diphenyl, and (*b*) the other between the diazo-compound and the alcohol leading to the formation of benzene, the latter probably conditioned by the prevention of the acidity of the medium. If this view be correct, the acid set free in reaction (*b*) would combine with zinc and liberate hydrogen, which ought to reduce one-half of the aldehyde to alcohol. But this, of course, would not be true in the cases where alkalis were present, so there ought to be only one-half the percentage of aldehyde formed in the cases when zinc-dust was present as where the decompositions were made in the presence of alkalis. But the determinations of the paraldehyde were not sufficiently accurate in these cases to justify conclusions in regard to the point. A careful study of the action of these diazo-compounds upon water in the presence of zinc-dust would probably throw light upon this question. For if there be the two reactions, one should give diphenyl and the other phenol. Until further facts bearing upon this question are accumulated the question must remain open.

It will be seen that more diphenyl is formed in those cases where methyl alcohol and the diazo-compound are decomposed in the presence of alkalis and zinc-dust, than in the corresponding cases where ethyl alcohol was used. For the preparation of diphenyl in large quantities I would suggest the decomposition of diazo-benzene nitrate and methyl alcohol in the presence of sodium carbonate.

By comparing the results obtained in the two cases where diazo-benzene nitrate was decomposed with dilute ethyl alcohol it will be observed that the one which was diluted with 10 per cent. of water formed diphenyl, while the one diluted with 30 per cent. of water did not form the diphenyl. It would appear, therefore, that the presence of large quantities of water is unfavorable to the formation of the diphenyl.

The formation of diphenyl by the decomposition of diazo-benzene nitrate in the presence of the sodium alcoholates, alkalis, and zinc-dust appears to be entirely similar to the formation of this compound by the action of zinc-dust on diazo-benzene sulphate, as described by Gatterman.[1]

[1] Ber. d. chem. Ges. **23**, 1226.

Conclusions.

The results which have been obtained in the course of this work justify, I think, the following conclusions:

1. When diazo-benzene nitrate is decomposed with methyl alcohol either at the room temperature or at the boiling-point of the alcohol, only the alkoxy product is formed.

2. Ortho-nitrophenol was also formed, probably by a molecular rearrangement of the diazo-benzene nitrate, with the loss of nitrogen, and then was converted into 2:4-dinitrophenol by the action of the nitric acid set free in the course of the reaction, partially while standing in the cold, and completely while heating to distill off the alcohol and anisol.

3. Para-nitrophenol, when formed, was shown to be due to the presence of a small amount of water in the alcohol, first forming phenol, and then, by the action of the nitric acid present, forming both ortho- and para-nitrophenols.

4. In the case of the decomposition of diazo-benzene nitrate with ethyl alcohol, it was shown that an elevated temperature apart from pressure increased the alkoxy reaction, while a lower temperature increased the hydrogen reaction.

5. The presence of a small amount of water increased the ethoxy product.

6. In the decompositions of diazo-benzene nitrate with methyl and ethyl alcohols it was shown that in general the presence of an excess of alkalis led to the hydrogen reaction.

7. In the decompositions of diazo-benzene nitrate and sulphate with methyl and ethyl alcohols, the presence of an excess of zinc-dust led to the hydrogen reaction.

8. The decomposition of diazo-benzene nitrate with a solution of sodium methylate in methyl alcohol, and of sodium ethylate in ethyl alcohol, gave diphenyl and benzene.

9. In the three preceding cases there appear to be two reactions, one between the diazo-salt and the neutralizing agent, giving the diphenyl reaction, and the other between the diazo-salt and the alcohol, giving the hydrogen reaction. The latter reaction was possibly due to the prevention of the acidity of the medium.

10. The decomposition of diazo-benzene sulphate with methyl alcohol gave entirely the alkoxy product.

RESEARCHES UPON THE PHENOMENA OF OXIDATION AND CHEMICAL PROPERTIES OF GASES.

By Francis C. Phillips.

[*Continued from page 187.*]

II.—Qualitative Reactions of Gases.

The recognition of any gas in a complex mixture is still a matter of difficulty in many cases, although in a few instances methods of identification are coming to be well known. Serious difficulties oppose all attempts at a system of qualitative analysis of gas-mixtures. There are but few groups of gases (if the name "group" be understood to include all gases chemically alike); moreover, the members of a group exhibit much closer relationships than are to be found among the metals of any one of the groups of Fresenius. The following classification of gases has been found convenient for purposes of study:

Group 1. Hydrogen.

Group 2. Carbon monoxide.

Group 3. Methane, ethane, propane, the butanes, etc.

Group 4. Ethylene, propylene, trimethylene, the butylenes, etc.

Group 5. Acetylene, allylene, etc.

Group 6. Sulphur compounds: Hydrogen sulphide; methyl hydrosulphide, $(CH_3)SH$; methyl sulphide, $(CH_3)_2S$; carbon oxysulphide, COS; carbon bisulphide.

Group 7. Carbon dioxide.

Unclassified: Nitrogen; oxygen.

In a study of the kind proposed, it is of importance to take into account not only gases that are permanent under ordinary conditions, but also vapors of liquids which are liable to occur in small quantities, such as carbon bisulphide, benzene, several of the lower paraffins and olefines, etc.

Methods Employed.

In the case of reactions between gases and solid substances, the solid to be tried was placed in a glass tube of ½-in. diameter, which could then be heated to any given temperature in the iron oven previously described, while the gas was caused to stream through the tube. In the case of reactions in solution, two methods were used:

1. The gas was caused to flow through a capillary tube into the solution contained in a test-glass. The escaping gas could then be led into a second and, if necessary, a third test-glass in order to ascertain the action of the solution used in the first test-glass.

2. The gas was collected in glass-stoppered bottles over water, a small quantity of a solution introduced by means of a tap-funnel with the lower end of its stem bent upward, then the bottle closed and kept inverted at any given temperature for sufficient length of time (usually from a few days to several months) to ascertain if a reaction had occurred. The former method answers well for gases which are easily controlled in a slow, continuous stream and obtainable in large quantity. The latter method is more economical as regards the gas to be used, and is better suited to gases where some slight but difficultly removable impurity is suspected to occur of a character liable to affect the regeant—such as the traces of hydrocarbons present in hydrogen made from zinc and sulphuric acid. In such cases the smaller the volume of gas to be used in a trial the better. A reaction may usually be obtained with from 20 to 50 cc. of gas. Small bottles having well-ground, flat-topped glass stoppers answer well, as they may be kept standing inverted and may, if heat is to be applied, be placed inverted in boiling water. It is hardly necessary to add that, when inverted, such bottles may be used to hold gas in contact with a reagent for long periods without danger of loss.

Hydrogen.

Hydrogen for the following experiments was prepared and purified as already described.[1] Reactions were tried in bottles, and by causing the gas to bubble through the solutions, as just detailed.

1.—*Reactions in Solution.*

Reagent.	Reactions.
Palladium chloride.....	The solution is slowly but completely reduced, cold or at 100°. The precipitated palladium usually collects as a black powder. Sometimes it is deposited as a film on the glass.
Platinum chloride[2].....	Very slow but complete reduction, cold or at 100°. The reduced metal appears as a black powder.

[1] Page 165. [2] Mendeléeff: Principles of Chemistry, vol. II, p. 353.

Gold chloride	Unchanged.
Silver nitrate	Unchanged if the fluid contains a trace of free nitric acid.
Ammoniacal silver nitrate	Slowly reduced, the silver appearing as a black powder.
Iridium chloride	Unchanged.
Rhodium chloride	Unchanged.
Potassium ruthenate	Slowly reduced. The orange color of the fluid disappears and metallic ruthenium is precipitated as a black powder.
Cerium dioxide dissolved in dilute sulphuric acid.	Unchanged.
Potassium permanganate,[1] neutral.	Extremely slow reduction, the purple color changing to brown.
Permanganate, acidulated with sulphuric acid.	Bleached slowly.
Permanganate, alkaline	Slowly changes to brown.
Potassium bichromate, acidulated with sulphuric acid.	Unchanged, cold or at 100°.
Mercuric chloride	Unchanged.
Osmic acid	Unchanged. Prolonged contact in bright light yields traces of reduction after two or three weeks.
Ferric chloride	Unchanged cold. Traces of reduction to ferrous chloride after heating for several hours at 100°.
Potassium ferricyanide	Unchanged.
Ruthenium chloride	Unchanged.
Nitric acid, fuming[2]	Unchanged.

Comments.—Russell[3] states that hydrogen reduces silver-nitrate solution, nitric acid being at the same time reduced to nitrous acid. Pellet[4] finds that this reduction is due to the silver salt containing silver oxide in excess, but that perfectly neutral silver nitrate is not altered. In a series of experiments I have obtained results corroborating those of Pellet. Silver nitrate containing a minute trace of free nitric acid is not altered by hydrogen. If some freshly precipitated and washed silver oxide is digested with solution of silver nitrate, and the liquid then filtered, it will have an alkaline reaction towards litmus and is slowly reduced by

[1] Meyer and Askenasy [Ann. Chem. (Liebig) **269**, 56 (1892); Ber. d. chem. Ges. **25**, 410 (Ref.)] find that electrolytic hydrogen reduces potassium permanganate.
[2] Winkler: Ztschr. anal. Chem. **28**, 269 (1889).
[3] J. Chem. Soc. **27**, 3 (1874).
[4] Compt. Rend. **78**, 1132.

hydrogen. Boiling the solution with silver oxide increases its alkalinity and also its sensitiveness towards hydrogen. As a reagent for the recognition of hydrogen, it is better that the solution of silver nitrate should be slightly basic (alkaline).

As regards the action of hydrogen upon ferric chloride, it should be said that mere traces of ferrous chloride are produced, as indicated by a faint change of color upon addition of potassium ferricyanide.

Free hydrogen has, therefore, a considerable reducing power for some of the more easily reducing metallic salts, which is intensified in some cases by heating to 100°.

It is convenient to distinguish between three classes of gas-reactions as regards intensity:

Reactions of the first class, in which a change is prompt and quantitative in its results, *e. g.* when carbon dioxide is brought into contact with soda solution.

Reactions of the second class, in which a change is slow but no less complete in a somewhat longer interval of time; *e. g.* the reduction of platinum-chloride solution by hydrogen.

Reactions of the third class, in which a change is not recognizable until after a considerable interval of time, and the products appearing then are only found in traces, such as the reduction of ferric chloride by hydrogen.

None of the preceding reactions of hydrogen appear to fall under the first class. Nearly all are of the second class. That reactions such as I have called of the third class should occur is difficult of explanation, and it is questionable whether a parallel is to be found in the case of ordinary reactions of metallic salts, *e. g.* precipitation of traces of ferrous sulphide in ferrous chloride solution by hydrogen sulphide, or calcium oxalate by ammonium oxalate in dilute acid solution, where a change in the proportion of free acid or alkali may cause the precipitation to become complete. The reduction of ammoniacal silver solution by hydrogen cannot be materially accelerated by increase of ammonia or other change in the conditions, and thus remains a typical reaction of the third class, no matter how it is carried out.

2.—*Reactions at High Temperatures.*

The heat of formation of hydrogen chloride being high (22 calories), it seemed probable that hydrogen should reduce the

chlorides of many of the metals at moderate temperatures. Small quantities of metallic chlorides were heated in a slow current of hydrogen in a glass tube in the iron oven. The following reactions were observed:

	Temperatures of Reduction.
Ruthenium chloride, anhydrous	190°.
Gold chloride (obtained by evaporation of a solution of gold in *aqua regia* to dryness).	Reduced at 150°.
Rhodium chloride, anhydrous	200°.
Platinum chloride (obtained by evaporation of the solution of platinum in *aqua regia* to dryness).	Reduced with evolution of water and hydrogen chloride below 80°.
Palladium chloride	Reduced cold.
Silver chloride	270°–280°.
Silver bromide	330°–360°.
Silver iodide	350°–370°.
Mercuric iodide	Volatile without reduction.

In the above experiments the hydrogen, after passing the heated metallic chloride, was conducted into dilute silver solution and the temperature observed at which a precipitation occurred. The reduction of palladium chloride occurs at the ordinary temperature. It is an exothermic change, as the following equation shows:

$$2PdCl_2 + 5H = Pd_2H^1 + 4HCl$$
$$-(2 \times 40 \text{ cal.}) + 9.4 \text{ cal.} + (4 \times 22 \text{ cal.})$$

Hence the heat of the completed reaction will be 17.4 calories.

If hydrogen be passed over dry palladium chloride contained in a glass tube, an immediate reduction to metallic palladium occurs, attended by evolution of hydrochloric acid. The reaction begins and is completed without application of external heat, the temperature of the mass becoming very high, as the above equation would indicate. The production of hydrogen chloride in this reaction renders palladium chloride a reagent of great sensitiveness for the recognition of free hydrogen in gas-mixtures. In order to study the reaction more fully it was necessary to prepare pure, dry palladium chloride. When a solution of palladium in *aqua regia* is evaporated to dryness, brown amorphous crusts are formed which are very imperfectly soluble in water or hydrochloric acid. Analyses were made of the compound so obtained, but the results showed varying amounts of chlorine, and it was

[1] The composition of palladium hydride is probably Pd_2H, according to Mendeléef: Principles of Chemistry, vol. II, p. 355.

evident that the salt had been partially decomposed during the evaporation. In order to obtain pure palladium chloride the following method of preparation was adopted:

Palladium dissolved in *aqua regia* was heated for several days in a covered beaker over the water-bath. Hydrochloric acid was added from time to time to insure the destruction of any lower oxides of nitrogen. The solution was then evaporated to dryness, and the residue heated to 180° in a glass tube through which a current of dry hydrogen chloride was passed. The excess of hydrogen chloride was then expelled by a stream of carbon dioxide, and after the escaping carbon dioxide was found to carry with it no more hydrogen chloride the compound was considered pure. Hydrogen was now passed through the tube and into standard soda solution. The palladium chloride was then reduced, and the resulting hydrogen chloride absorbed by the soda. The chlorine was determined volumetrically. Two analyses were made. The results showed the salt to consist of palladium dichloride.

Experiments undertaken for the purpose of comparison of the properties of the two preparations demonstrated that palladium chloride prepared by the method above detailed is a much more sensitive reagent towards free hydrogen than the compound obtained on merely evaporating to dryness a solution of palladium chloride on the water-bath. So delicate is the reaction that a neutral gas, such as nitrogen, containing $\frac{1}{20}$ of 1 per cent. of free hydrogen, will rapidly give an indication when passed over the palladium chloride and into a solution of silver nitrate. It is absolutely necessary, especially where traces of hydrogen are suspected, that the gas should be dry, as moisture is liable to condense with the hydrogen chloride in drops, and thus the hydrogen chloride may be prevented from reaching the silver-nitrate solution.

Ethylene reduces palladium chloride at temperatures above 100°. Palladium chloride heated in an inert gas, such as carbon dioxide, was found to yield chlorine at about 250°. In presence of oxygen the case is very different. Palladium chloride heated in dry air loses chlorine readily at 160°, being apparently converted into an oxychloride. After long-continued heating to 100° in air, chlorine in minute traces is set free and recognizable by silver nitrate containing some ferrous sulphate. If air containing any hydrocarbon (paraffin, olefine or acetylene) be led over gently heated palladium chloride a decomposition occurs at once.

The palladium salt is reduced and hydrogen chloride is promptly set free. Alcohol, ether, and benzene vapor cause similar results. Repeated trials have shown that less than 0.1 per cent. of hydrogen in air may be recognized by the reaction above described if the temperature of the palladium chloride is not increased above 50° C. If the temperature rises to 100°, chlorine will be evolved from palladium chloride by the action of air alone, as may be easily shown by causing the air to bubble through silver-nitrate solution containing a little ferrous sulphate (free chlorine is not easily detected by silver nitrate alone, and may bubble through it unabsorbed and unrecognized).

The reduction of anhydrous ruthenium chloride by hydrogen is curiously influenced by the presence of oxygen. Ruthenium chloride was reduced by pure hydrogen at 190°. In another experiment, using a mixture of hydrogen 4 volumes and air 6 volumes, no hydrochloric acid was produced, even on heating to 320°. The following is the most convenient method of applying the test:

The gas, previously dried (1) by calcium chloride, and (2) by phosphoric anhydride, is conducted through a narrow tube to the bottom of a dry test-tube containing about 0.2 gram of palladium chloride. The test-tube has a rubber cork with two holes. Through a second tube the gas escapes and passes into a solution of nitrate of silver. The test-tube may remain cold, but, in the absence of oxygen or air, it is better to immerse in water at 40° or 50°, provided no hydrocarbons likely to reduce palladium chloride are suspected. The palladium chloride may be placed in a glass tube of ½-in. bore, with asbestos plugs to prevent its becoming displaced by the gas stream, and then the tube connected with the vessel containing silver nitrate solution. If traces only of hydrogen are to be tested for, oxygen must be completely removed by prolonged contact with pyrogallol and soda, or, better, with green-vitriol solution and milk of lime. The latter method for the removal of oxygen is to be preferred, although the action is much slower.

Palladium oxidized by heating in air is quickly reduced by free hydrogen. If a gas containing hydrogen is conducted over palladium oxide and then through a narrow tube containing a very small quantity of a mixture of potassium ferricyanide and green vitriol in fine powder, the moisture, formed in the reaction between

the hydrogen and the palladium oxide, will change the color of the powder to blue.

Silver oxide is reduced by hydrogen at 100°.[1]

Iodic acid is not reduced by hydrogen a 250°, *i. e.* at a temperature approaching the point at which iodic acid dissociates (distinction between hydrogen and carbon monoxide).

Iridium dioxide undergoes a reduction to metal in contact with free hydrogen. The reduction occurs in the cold and is attended with brilliant scintillations. By employing a moisture-indicator it is possible, by the help of this reagent, to recognize minute quantities of hydrogen.

In point of delicacy the palladium-chloride reaction is superior to all others. Experiments are in hand with a view to the utilization of this reaction for the quantitative determination of hydrogen. The occlusion of hydrogen by the reduced palladium and consequent loss have, so far, prevented the use of this reaction for quantitative work.

Methane.

Preparation.—From methyl iodide by the method of Gladstone and Tribe.[2]

Methane, the typical member of the paraffin group, is of all hydrocarbons (with the possible exception of ethane) the most stable towards reagents.

1.—*Reactions in Solution.*

Reagent.	Reactions.
Palladium chloride	The solutions of these salts are unaltered by prolonged contact with methane, cold or at 100°.
Platinum chloride	
Gold chloride	
Silver nitrate	
Ammoniacal silver nitrate	
Iridium chloride	
Rhodium chloride	
Cerium dioxide dissolved in sulphuric acid	
Potassium bichromate acidulated with sulphuric acid	
Mercuric chloride	
Ferric chloride	
Ruthenium chloride	

[1] Darvydowa: J. russ. phys.-chem. Ges. 1888, 362; Ber. d. chem. Ges. **21**, 442 (Ref.) (1888).

[2] See p. 172.

Potassium permanganate (2-per cent. solution) is unchanged, whether neutral or acidulated by sulphuric acid.

Osmic acid is not reduced by methane in the cold.

Potassium ferricyanide is unchanged.

Peroxide of hydrogen mixed with lime-water remains clear, proving that no oxidation to carbon dioxide occurs.

Calcium-hypobromite solution remains free from any deposit of calcium carbonate.

Bromine-water is not decolorized after prolonged contact.

Chlorine attacks methane only at a temperature considerably above 100°. A mixture of methane and chlorine was exposed over water to bright sunlight on a July day without undergoing any noticeable contraction in volume or change of color.[1]

Potassium rutheniate is slowly reduced with separation of metallic ruthenium.

If methane is conducted into strong sulphuric acid to which crystals of permanganate have been added, immediate oxidation to carbon dioxide occurs, as proved by the action upon lime-water (in this experiment stoppers made of plaster of Paris were used). This reaction towards permanganic anhydride is a very delicate one. All hydrocarbon gases yield a similar result.

2.—*Reactions at High Temperatures.*

Ferric oxide (prepared by ignition of ferric nitrate) heated in a glass tube over a strong Bunsen-burner flame underwent very slow and incomplete reduction, some carbon monoxide being formed in addition to carbon dioxide. Iodic acid (crystals) is not reduced by methane on heating nearly to its temperature of dissociation (250°). Neither iodine vapors nor carbon dioxide is formed. The action of methane upon the chloride, bromide, and iodide of silver was tried by the same method followed in the case of hydrogen—these substances contained in a glass tube being heated in methane and the gas then conducted into silver-nitrate solution. The temperatures of decomposition were as follows:

	Temperature of Decomposition.
Silver chloride.....	At melting-point of barium chlorate (414°).
Silver bromide.....	Above melting-point of thallium iodide (439°).
Silver iodide.....	Slightly volatile without reduction.

[1] See experiments in "Chlorination of Methane."

The order of reducibility by hydrogen and by methane is the same, therefore, as in the case of the action of light, the chloride being the most easily reduced, the iodide the most stable.

Nickel chloride heated in natural gas (from Murrysville) underwent conversion into its nearly colorless, beautifully crystalline modification. An analysis made in the laboratory by Mr. H. T. Weed showed the composition of the salt to have been unchanged. At a dull-red heat reduction occurred, with liberation of carbon.

Ethane.

This hydrocarbon was prepared from ethyl iodide by the process of Gladstone and Tribe, as described on p. 173.

1.—*Reactions in Solution.*

All the reagents used in the case of methane were tried. The reactions were so closely similar that a detailed statement is omitted as unnecessary.

Ethane exhibits the same stability as the other paraffins towards reagents in solution. Oil of vitriol containing crystals of potassium permanganate causes prompt oxidation to carbon dioxide. Potassium ruthenate is quickly reduced with separation of metallic ruthenium.

2.—*Reactions at High Temperatures.*

Towards iodic acid, silver bichromate, and the various metallic oxides, ethane closely resembles methane in its reactions.

Propane.—Reactions.

Experiments with propane made by the method of Gladstone and Tribe from propyl iodide, led to results closely similar to those obtained with ethane and methane.

As already stated, propane is somewhat more easily oxidized than the paraffins lower in carbon. In a series of trials, using the same reagents in solution as mentioned in the preceding experiments, no reactions were obtained which would serve to distinguish between propane and methane or ethane. The results are therefore omitted.

Isobutane.—Reactions.

This hydrocarbon, prepared by the method of Gladstone and Tribe from isobutyl iodide, was found closely to resemble in its

reactions the paraffins already described. It is characterized, however, by a lower oxidation-temperature, as already stated in regard to the experiments with palladium asbestos.

Heptane.

Heptane obtained from "theoline"[1] was found to have the same general chemical properties as methane. Even cerium dioxide, osmic acid, gold chloride and potassium permanganate are unaltered by prolonged contact with the liquid hydrocarbon. Heptane seems in fact to be almost, if not quite, as stable as methane towards reagents in solution.

The paraffins as a group are, in the main, so proof against reactions that we can do little more than remove all other hydrocarbons by suitable reagents and then test for paraffins by combustion over oxide of copper to carbon dioxide and water. This, of course, leaves the nature of the individual paraffins undetermined. Spongy palladium, heated in air so as to became partially converted to palladium oxide and transferred to an atmosphere of methane or other paraffin, undergoes a reduction. The reduced metal then combines with the carbon of the hydrocarbon.[2] This carbide heated in air or oxygen yields carbon dioxide. The production of carbon dioxide in this case may be utilized as a test for hydrocarbons in a gas-mixture, provided no free oxygen is present. The carbide of palladium, formed by the above method, dissolves in *aqua regia* (containing but little nitric acid) with a camphor-like odor.

Olefines: Ethylene.

For preparation, see p. 176. The method of Erlenmeyer and Bunte was used. It is necessary for the purpose of studying its reactions to purify the gas from traces of the vapors of alcohol and ether by prolonged digestion with sulphuric acid.

1.—*Reactions in Solution.*

Reagents.	Reactions.
Palladium chloride.....	Quickly reduced, the metal appearing as a black powder. No carbon dioxide is formed.
Platinum chloride.....	Unchanged.

[1] See p. 175.

[2] Graham-Otto: Vol. III, p. 995; Wilm: Ber. d. chem. Ges. 25, 220 (1892).

Gold chloride	Extremely slow reduction, the gold appearing as a brown powder. No carbon dioxide.
Gold chloride in excess of potassium hydroxide.	Extremely slow reduction.
Iridium chloride	Unchanged.
Ruthenium chloride	After prolonged contact (several days) the solution is bleached. No deposition of metal occurs.
Rhodium chloride	Unchanged.
Silver nitrate	Unchanged.
Silver nitrate in ammoniacal solution.	Unchanged.
Potassium permanganate, neutral solution.	Quickly turns brown.
Potassium permanganate acidulated with sulphuric acid.	Quickly bleached.
Potassium permanganate crystals in concentrated sulphuric acid.	Prompt oxidation to carbon dioxide.
Potassium bichromate acidulated with sulphuric acid.	No change of color, cold or at 100°.
Osmic acid	Quickly reduced, with separation of metal as a black powder.
Potassium rutheniate	Quickly reduced, with separation of metal.
Ferric chloride	No change, cold or at 100°.
Calcium hypobromite containing excess of lime-water.	No precipitation of calcium carbonate, and hence no oxidation to carbon dioxide.
Potassium ferricyanide	Unchanged.
Bromine-water	Rapid but incomplete absorption.
Peroxide of hydrogen	No oxidation to carbon dioxide.

2.—*Reactions at High Temperatures.*

Silver oxide is reduced by ethylene with simultaneous formation of silver carbonate at 140°.[1] Palladium chloride (dry) is reduced at about 140°. Iodic acid is reduced with liberation of iodine at about 270°.

Comments.—As is well known, bromine-vapor and ethylene combine to form an oily liquid by the reaction so characteristic of the olefine group. Winkler[2] has shown that the absorption of ethylene by bromine is incomplete, and that the contraction in

[1] Darvydowa: J. russ. phys.-chem. Ges. 1888, 369; Ber. d. chem. Ges. **21**, 442 (Ref.) (1888).
[2] Ztschr. anal. Chem. **28**, 369 (1889).

volume is by no means proportional to the volume of the ethylene present.

I have tried experiments upon ethylene prepared from alcohol and from ethylene dibromide (by the action of zinc powder), and the results show that a considerable residue of hydrocarbon remains unabsorbed after prolonged contact with bromine-water in sunlight. The residual gas, on being mixed with air and passed over ignited oxide of copper, gave carbon dioxide and water at the outset.

The reaction between ethylene and palladium chloride in solution is of the second class and complete, the gas being rapidly absorbed. Palladium is deposited as a black powder, but no trace of oxidation to carbon dioxide occurs. The reaction is almost the same in the cold and at 100°. The gas escaping from the palladium-chloride solution (after complete reduction to metallic palladium) produces no precipitate in lime-water. The reaction between palladium chloride and ethylene leads to the production of aldehyde.[1] Of especial interest in this connection is a statement by Berthelot,[2] that ethylene is oxidized to aldehyde by the action of chromic-acid solution at 120°.

Gold chloride produces a similar result, the metal being slowly reduced. As in the case of palladium chloride, no carbon dioxide is formed.

Rhodium chloride is remarkably stable towards ethylene (and other olefines): after three months' contact with the gas, no trace of reduction was observed.

Potassium permanganate (in weak solution) has been shown by Wagner[3] to convert olefines on digestion (cold) into glycols. The reaction may serve as a mode of preparing glycols, but could only in exceptional cases be utilized as a gas-reaction.

Chromic-acid mixture is said to be reduced by ethylene.[4] In repeated experiments I have failed to show that chromic acid undergoes reduction by ethylene. No carbon dioxide is formed, the color of the solution remains unchanged, and no absorption occurs on prolonged contact of ethylene with a 10-per cent. solution of chromic acid in a eudiometer. Similar results were

[1] A study of the changes here involved is yet in hand.

[2] Compt. Rend. **68**, 334.

[3] Ber. d. chem. Ges. **21**, 1230 (1888).

[4] Chapman and Thorp: J. Chem. Soc. **19**, 491 (1866); Watt's Dic. (1st Ed.), 1st Supp., p. 602.

obtained in using potassium bichromate acidulated by sulphuric acid. Carbon dioxide could not be detected on passing ethylene through a solution of chromic acid at 100°.

Potassium rutheniate, an extremely sensitive reagent, loses its orange color rapidly and deposits metallic ruthenium.

Peroxide of hydrogen is said by Berthelot to convert ethylene into glycol. This has apparently no significance as a gas-reaction.

The reduction of palladium-chloride solution, if *not* attended by evolution of carbon dioxide, is an evidence of the presence of an olefine (and probably ethylene as the commonest of the olefines) in a gas-mixture.

Sulphuric acid does not absorb ethylene in the cold, but the absorption is rapid at a temperature of 160°.

Propylene.

Preparation.—From allyl iodide by the action of zinc (see p. 179).

1.—*Reactions in Solution.*

Propylene, in its reactions towards the various reagents, resembles ethylene so closely that no important differences can be mentioned.

Reagents.	Reactions.
Palladium chloride	Reduction is prompt and complete, the gas undergoing rapid absorption. If mixed with nitrogen (as an inert diluent) and conducted into lime-water, after passing through the palladium-chloride solution, it is easily shown that no oxidation to carbon dioxide is produced by the palladium chloride. The same is true if air is used instead of nitrogen.
Platinum chloride	Unchanged, cold or at 100°.
Gold chloride	No change, cold, until after prolonged contact or on heating to 100°.
Silver nitrate	Unchanged.
Silver nitrate in ammoniacal solution	Unchanged.
Iridium chloride	Unchanged, cold or at 100°.
Ruthenium chloride	Unchanged.
Rhodium chloride	Unchanged.

Potassium rutheniate	Traces of reduction after twenty-four hours.
Cerium dioxide in dilute sulphuric acid.	No change, cold or at 100°.
Potassium permanganate	Slowly turns brown.
Potassium permanganate acidulated with dilute sulphuric acid.	Quickly bleached.
Potassium permanganate crystals in concentrated sulphuric acid.	Prompt oxidation to carbon dioxide.
Chromic acid	Unchanged.
Osmic acid	Quickly reduced, with precipitation of metal as a black powder.
Ferric chloride	Unchanged, cold or at 100°.
Bromine-water	Incomplete absorption, even after prolonged contact.
Peroxide of hydrogen	No carbon dioxide formed.
Ferricyanide of potassium	Unchanged. Not reduced to ferrocyanide.
Calcium hypobromite containing excess of lime-water.	Unchanged.

Propylene is not absorbed by sulphuric acid in the cold.

2.—*Reactions at High Temperatures.*

As regards reducing action upon metallic oxides, no important properties distinguishing propylene from ethylene can be named.

Propylene conducted over crystals of iodic acid contained in a glass tube heated in the oven, undergoes oxidation, yielding iodine vapors and carbon dioxide at a temperature approximating that of dissociation of the iodic acid.

Comments.—Towards reagents in solution, propylene appears in some cases to possess slightly greater stability than ethylene. This is especially the case with gold chloride and potassium rutheniate. Like ethylene, it is not oxidized to carbon dioxide by any of the reagents used in solution, with the exception of potassium permanganate in concentrated sulphuric acid. Experiments with bromine-water have led to the same results as in the case of ethylene. The absorption is decidedly incomplete.

Isobutylene.

This gas was prepared from isobutyl iodide by the method described on p. 181. The reactions were in the majority of cases perfectly similar to those of ethylene and propylene.

1.—*Reactions in Solution.*

Reagents.	Reactions.
Palladium chloride	Quickly reduced. No carbon dioxide formed.
Platinum chloride	Unchanged.
Gold chloride	Quickly reduced. No carbon dioxide is evolved in the cold or at 100°.
Silver nitrate	Unchanged.
Ammoniacal silver nitrate	Unchanged.
Rhodium chloride	Unchanged.
Potassium rutheniate	Quickly reduced.
Cerium dioxide in dilute sulphuric acid.	Rapidly bleached.
Potassium permanganate, neutral	Turns brown.
Potassium permanganate acidulated with dilute sulphuric acid.	Quickly bleached.
Potassium permanganate crystals in sulphuric acid.	Prompt oxidation of the gas to carbon dioxide.
Chromic acid	Unchanged.
Osmic acid	Quickly reduced, metallic osmium being precipitated.
Ferric chloride	Unchanged.
Bromine-water	Promptly but incompletely absorbed.
Peroxide of hydrogen	No formation of carbon dioxide.
Potassium ferricyanide	Unchanged.
Calcium hypobromite containing excess of lime-water.	Unchanged.
Iodine dissolved in potassium-iodide solution.	Quickly bleached.
Mercurous nitrate	Precipitation of a gray powder which consists of (or changes into) metallic mercury.
Sulphuric acid of 1.8 specific gravity	Does not absorb isobutylene in the cold.

2.—*Reactions at High Temperatures.*

Experiments upon the reducing action of isobutylene upon metallic oxides at high temperatures did not develop any characteristic differences.

Iodic acid was reduced by isobutylene at 89°, with formation of carbon dioxide and free iodine.

Comments.—Isobutylene prepared by Puchot's method from isobutyl alcohol, causes a white precipitate in ammoniacal silver-

nitrate solution, while that prepared from isobutyl iodide and potash exerts no such action.

The reaction towards mercurous nitrate (of the second class) distinguishes between isobutylene and the olefines lower in carbon. In its bleaching action upon iodine dissolved in potassium-iodide solution, isobutylene differs from both ethylene and propylene and also in the fact that it bleaches cerium dioxide in sulphuric-acid solution. It is not oxidized to carbon dioxide by any of the reagents in solution, with the exception of permanganate of potash in strong sulphuric acid.

Trimethylene.

This hydrocarbon was prepared from trimethylene bromide by the action of zinc.[1] The gas was purified by sulphuric acid and by digestion with dilute potassium-permanganate solution.

1.—*Reactions in Solution.*

Reagents.	Reactions.
Palladium chloride	Reduced with extreme slowness. No carbon dioxide is formed. The reaction requires a much longer time than in the case of the olefines proper.
Platinum chloride	Unchanged, cold or at 100°.
Gold chloride	Unchanged, cold or at 100°.
Silver nitrate	Unchanged.
Ammoniacal silver nitrate	Unchanged.
Iridium chloride	Unchanged, cold or at 100°.
Rhodium chloride	Unchanged, cold or at 100°.
Potassium rutheniate	Traces of reduction after prolonged contact (reaction of the third class).
Cerium dioxide dissolved in dilute sulphuric acid.	Unchanged.
Potassium permanganate, neutral	Unchanged.
Potassium permanganate acidulated with dilute sulphuric acid.	Unchanged.
Potassium permanganate crystals in sulphuric acid.	Immediate oxidation to carbon dioxide.
Chromic acid	Unchanged.
Ferric chloride	Traces of reduction to ferrous chloride after twenty-four hours (reaction of the third class).
Bromine-water	Extremely slow absorption.

[1] See p. 180.

Peroxide of hydrogen	Unchanged.
Potassium ferricyanide	Unchanged.
Calcium hypobromite in excess of lime-water.	Unchanged.
Iodine dissolved in potassium-iodide solution.	Unchanged.
Sulphuric acid, 1.8 specific gravity	The gas is not absorbed in the cold.

2.—*Reactions at High Temperatures.*

Iodic acid in crystals was reduced with formation of carbon dioxide at a temperature closely approximating the temperature of dissociation of the acid.

Comments.—The olefines are characterized by great stability towards oxidizing influences at temperatures below 100°, so that carbon dioxide is not evolved except in the case of the action of potassium permanganate in concentrated sulphuric acid. In several cases where destructive oxidation might be expected to occur, the olefines are converted into glycols (*e. g.* in the case of dilute potassium permanganate).

Trimethylene yields reactions similar to those of the true olefines, but is decidedly more stable towards many reagents. It does not reduce osmic acid, potassium permanganate or gold chloride. By these three reagents it is best distinguished from the true olefines.

It may be mentioned that ether-vapor, which so frequently contaminates the olefines, does not reduce palladium-chloride solution.

Carbon Monoxide.

This gas was prepared by heating a mixture of pure oxalic acid and sulphuric acid and purified by caustic soda solution.

1.—*Reactions in Solution.*

Reagents.	Reactions.
Palladium chloride	Quickly reduced, with oxidation of carbon monoxide to carbon dioxide. The reaction is very delicate in strongly acid solutions or in solutions of the pure, dry chloride in water.
Platinum chloride	Carbon monoxide is oxidized to carbon dioxide, cold or at 100°. A reduction of the platinum salt to a lower chloride occurs, the solution assuming a darker color. After prolonged contact (several days or even weeks) an incomplete precipitation sometimes, but not always, occurs.

Gold chloride	Quickly reduced to metallic gold in form of a brown powder, the carbon monoxide being rapidly oxidized to carbon dioxide, cold or at 100°.
Gold chloride in excess of potassium hydroxide.	Immediately reduced. Very delicate reaction (of the first class).
Silver nitrate	Unchanged.
Ammoniacal silver nitrate	Slow reduction to metallic silver, which separates as a black powder. The filtrate from the precipitated silver was found to contain nitrous acid (as a result of the action of the carbon monoxide on silver nitrate in ammonia) when tested by Griess' reaction.
Iridium chloride	Slowly reduced to metal.
Rhodium chloride	Unchanged, cold; slowly reduced at 100° (reaction of the third class).
Potassium rutheniate	Rapidly reduced. Metallic ruthenium separates as a black powder.
Cerium dioxide in dilute sulphuric acid.	Unchanged, cold or at 100°.
Potassium permanganate	Quickly reduced, whether in neutral, alkaline, or acid solution.
Chromic acid	No change of color occurs, but a trace of carbon dioxide is formed (reaction of the third class).
Osmic acid	Quickly reduced.
Ferric chloride	Ferrous chloride is produced in traces after prolonged contact.
Hydrogen peroxide	No oxidation to carbon dioxide.
Ferricyanide of potassium	Unchanged.
Calcium hypobromite containing excess of lime-water.	Unchanged.
Fuming nitric acid	Oxidation to carbon dioxide.

2.—*Reactions at High Temperatures.*

Iodic acid in crystals is reduced by carbon monoxide, yielding carbon dioxide and iodine vapors at 90°[1]. De La Harpe recommends this method for the recognition of carbon monoxide in air. As higher olefines reduce iodic acid at about the same temperature as carbon monoxide, it would be necessary to remove them. According to my experiments, it would be necessary also to remove

[1] De La Harpe: Chem. Ztg. **12**, 1726; Ztschr. anal. Chem. **28**, 391 (1889).

acetylenes, and the vapors of benzene and alcohol, inasmuch as these substances exert an action similar to that of olefines. The lower paraffins are without action up to temperatures at which iodic acid dissociates.

Potassium iodate in crystals is not reduced by carbon monoxide at the melting-point of barium nitrate (593°). Carbon monoxide undergoes a decomposition in presence of certain metals at high temperatures, according to the reaction:

$$2CO = CO_2 + C.$$

Nickel causes such a change to occur at 350°, a very small quantity of the metal serving to decompose a large volume of the gas.[1] Iron is said to cause a similar decomposition at 227°.[2] I have made the following experiment with palladium:

Palladium asbestos was heated in a porcelain tube in a slow stream of pure carbon monoxide, air having been expelled from the apparatus, previous to the heating, by means of the carbon-monoxide stream. At a moderately high temperature (it was below redness) carbon dioxide was produced in such quantity as to cause a strong reaction in lime-water.

Carbon monoxide reduces oxide of iron at 240°.[3]

Howe[4] states that incipient reduction of iron oxide by carbon monoxide occurs at 141°.

The temperature of reduction of oxide of iron by carbon monoxide is unquestionably much lower than in the case of methane and ethane.

Carbon monoxide is absorbed by soda-lime at a temperature of 200°–220°, yielding sodium formate. Moisture promotes the reaction.[5] The reaction is as follows:

$$NaOH + CO = HCOONa.$$

The change is checked at higher temperatures, hydrogen being liberated at 300°. The volatile formic acid easily liberated from the sodium formate (by decomposition and distillation with tartaric acid) may be recognized by its reducing action upon ammoniacal silver-nitrate solution. The purest caustic soda obtainable often contains substances of a reducing nature, and it is

[1] Mond, Lange and Quincke: J. Chem. Soc. **57**, 749 (1890).
[2] Bell: Chemical Phenomena of Iron Smelting, pp. 80, 81.
[3] *Ibid.* p. 80.
[4] Eng. and Min. J. **50**, 426.
[5] Merz and Weith: Ber. d. chem. Ges. **13**, 718 (1880).

necessary to use soda free from such impurities. If the formate of soda extracted by water from the soda-lime be acidulated and distilled, the formic acid obtained in the distillate may be tested for by silver solution.

Carbon monoxide is oxidized to carbon dioxide by steam alone, at about 600°.[1]

Action of Carbon Monoxide upon Methane (Natural Gas) at High Temperatures.

According to Odling,[2] the following reaction occurs when methane and carbon monoxide are passed through a heated tube:

$$CH_4 + CO = H_2O + C_2H_2.$$

Natural gas from Murrysville, Pa., having the following composition, was used in the experiment detailed below:

Methane	95.40
Carbon dioxide	0.20
Nitrogen	4.40
	100.00

Natural gas mixed with carbon monoxide in the proper proportion (both being carefully freed from carbon dioxide) was passed through a porcelain tube filled with bone-black (previously purified from calcium salts by muriatic acid). The tube was heated by a coke fire with a strong draft to a temperature which finally caused softening of the porcelain tube. The escaping gases were passed (1) into lime-water, (2) into ammoniacal cuprous chloride. No trace of a red precipitate appeared in the cuprous chloride solution such as would have formed if acetylene had been produced. On replacing the cuprous-chloride solution by bromine-water, no oily drops collected in the fluid such as would have formed if an olefine had been produced. I have failed, therefore, to show that methane in contact with carbon monoxide at a high temperature gives rise to the formation of an unsaturated hydrocarbon.

Comments.—The best reagent for the recognition of carbon monoxide is palladium chloride. The reaction towards this salt in solution forms the basis of the well-known method for the quantitative determination of carbon monoxide. Although slow, the reaction is extremely delicate. It is accelerated by warming to

[1] Naumann and Pistor: Ber. d. chem. Ges. **18**, 2894 (1885).
[2] Watt's Dic. (1st Ed.), vol. I, p. 1111.

100°. Minute quantities of carbon monoxide in air may be recognized by the precipitation of metallic palladium from palladium-chloride solution. The precipitation often appears in the form of a lustrous metallic film of a dark-brown color coating the glass. My experiments upon the action of olefines show, however, that it is essential to the identification of carbon monoxide that the formation of carbon dioxide by the action of the palladium chloride be proved by means of lime-water or other indicator, as otherwise the reduction of the palladium salt may be due to a member of the olefine group. The air may be caused to flow slowly through palladium-chloride solution and then into lime-water. The tendency to undergo oxidation to carbon dioxide on the part of carbon monoxide, and the absence of such tendency on the part of the olefines when exposed to oxidizing influences at a temperature of 100° or below, serves as a most important criterion for the purpose of distinguishing between carbon monoxide and the olefine group. Winkler[1] has called attention to the value of palladium chloride as a reagent for the detection of carbon monoxide and has made many valuable suggestions.[2]

Platinum chloride is also a valuable reagent for the detection of carbon monoxide. Although oxidation to carbon dioxide occurs, no metal is precipitated unless the exposure to the gas be continued for several days, when traces of platinum appear. The solution assumes a darker color and a partial reduction results.

Gold-chloride solution is as energetic as palladium chloride in causing oxidation of carbon monoxide.

The reduction of ammoniacal silver-nitrate solution by carbon monoxide has been described by Berthelot.[3] Although chromic acid produces minute traces of carbon dioxide at 100° when carbon monoxide is conducted through its solution, my results do not confirm the statements of Ludwig,[4] according to whom, carbon monoxide may be determined by oxidation to carbon dioxide caused by chromic-acid solution.

The interesting compound formed by the direct union of carbon monoxide and platinum chloride[5] is not likely to prove of importance in connection with the study of gas-reactions.

[1] Ztschr. anal. Chem. **28**, 269 (1889).

[2] For a very convenient form of apparatus for the quantitative determination of carbon monoxide by palladium chloride, see Ellen Richards: This Journal **7**, 144.

[3] Compt. Rend. **112**, 597.

[4] Ann. Chem. (Liebig) **162**, 47 (1872).

[5] Pullinger: J. Chem. Soc. **59**, 598 (1891).

Among the reactions I have studied the most important for distinguishing between olefines and carbon monoxide are the following:

(1) The action of palladium chloride, which in the case of carbon monoxide yields carbon dioxide and in the case of ethylene yields no carbon dioxide. In both cases reduction of the palladium salt occurs.

(2) Ammoniacal silver nitrate is unaltered by olefines containing not more than four carbon atoms, but is reduced to metallic silver and ammonium nitrite by carbon monoxide.

(3) Platinum chloride yields carbon dioxide, but is not immediately reduced to metal by carbon monoxide. With ethylene no change occurs.

(4) Rhodium chloride is slowly reduced by carbon monoxide, but is unaltered by ethylene.

Among olefines, isobutylene is distinguished by its reducing action upon cerium dioxide and by its absorption of iodine in solution, the color of the latter being bleached.

Trimethylene, which is a saturated hydrocarbon, cannot be properly included among olefines, although isomeric with them. It is especially distinguished from the olefines proper by its stability towards neutral potassium permanganate and towards osmic acid. In almost all cases the reactions of trimethylene are much slower and less complete than those of the olefines.

[*To be continued.*]

Contributions from the Chemical Laboratory of Harvard College.

LXXXIII.—ON CERTAIN SUBSTITUTED CROTONOLACTONES AND MUCOBROMIC ACID.

By Henry B. Hill and Robert W. Cornelison.

[*Continued from p.* 213.]

α-Bromcrotonolactone.

Since the γδ-dibrompyromucic acid is as yet unknown, and the α-bromine atom of the αβ-dibromcrotonolactone seems always to

be first attacked by reagents, it was necessary to try some new method for the preparation of the α-bromcrotonolactone. It occurred to us that it was by no means impossible that it might be made from brommaleyl bromide, since the chloranhydrides of similar dibasic acids were known in several instances to yield lactones on reduction. We soon found on trial that our conjecture was correct. Hill and Sanger[1] had already shown that a crystalline body having the formula $C_4HBr_3O_2$, and yielding monobrommaleic acid when decomposed by water, could be made from $\beta\delta$-dibrompyromucic acid by the action of bromine in aqueous solution. This brommaleyl bromide we therefore prepared, although we modified slightly the method of preparation in that we dissolved the $\beta\delta$-dibrompyromucic acid in the requisite amount of a dilute solution of sodic carbonate, and added to this feebly alkaline solution slightly more than two molecules of bromine. We attempted to purify the product by distillation *in vacuo*, and found that it boiled without noticeable decomposition at 124°–125° under a pressure of 17 mm. The distillate remained liquid for a long time, and then but partially solidified with the separation of the original substance. The solid portion melted at 54°–55°, while the brommaleyl bromide, according to Hill and Sanger, melts at 55°–56°. The liquid portion was much more readily attacked by cold water than the original substance, and gradually dissolved, leaving about one-third its weight of the crystalline solid, which had been held in solution. In the aqueous solution was found monobrommaleic acid melting at 130°, and by evaporation monobromfumaric acid melting at 178° was obtained. These facts seem to us sufficient to show that we had in our hands two different bodies, each of which showed the properties of a brommaleyl bromide. The relation between these bodies will be more fully investigated. For the preparation of the α-bromcrotonolactone we found that no purification of the crude product was necessary.

The brommaleyl bromide is readily reduced by a solution of stannous chloride in strong hydrochloric acid, but the isolation of the lactone which is formed is difficult. Although it is volatile with steam, it distils slowly, remains dissolved in the distillate, and must be extracted from the dilute solution by ether. We have found it more convenient to use zinc and acetic acid for the

[1] Proc. Am. Acad. **21**, 166.

reduction. The brommaleyl bromide is suspended in one and a half times its weight of 80-per cent. acetic acid, and somewhat more than the calculated amount of zinc-dust added with careful cooling. The reaction is at first attended with great evolution of heat, and the zinc-dust must be added slowly. After the completion of the reaction the addition of water to the filtered solution precipitates but a small part of the lactone, and the solution must be thoroughly extracted with ether. The ethereal solution, when washed with a dilute solution of sodic carbonate and dried with calcic chloride, leaves upon distillation the beautifully crystalline α-bromcrotonolactone contaminated with but small amounts of oily impurities. The thoroughly pressed substance may most readily be purified by recrystallization from ether. This same α-bromcrotonolactone is also formed by the action of bromine in aqueous solution upon β-brompyromucic acid. As is the case with the analogous reaction by which $\alpha\beta$-dibromcrotonolactone is formed from $\beta\gamma$-dibrompyromucic acid, the yield is small, and we have as yet merely satisfied ourselves of the identity of the product through its physical properties.

0.2000 gram substance gave 0.2304 gram AgBr.

	Calculated for $C_4H_3BrO_2$.	Found.
Br	49.08	49.01

The α-bromcrotonolactone is readily soluble in alcohol or chloroform; somewhat more sparingly soluble in ether or benzol; sparingly soluble in cold carbonic disulphide, more readily in hot; and sparingly soluble in ligroïn. It dissolves quite freely in boiling water and distils slowly with steam. It crystallizes in long transparent prisms of adamantine luster, which melt at 77°. It dissolves in alkalies with a deep yellow color and the formation of an alkaline bromide. It also reduces argentic nitrate in ammoniacal solution on boiling. With aniline, when dissolved in dilute alcohol, it gives the well-crystallized α-phenylamidocrotonolactone. The α-bromcrotonolactone appeared to be identical with the body of like formula and the same melting-point which Hill and Sanger[1] obtained in small quantity as a by-product in the preparation of the dibrompyromucic acids by the action of alcoholic sodic hydrate upon pyromucic tetrabromide. Still their statements concerning the behavior of their substance toward

[1] Proc. Am. Acad. 21, 158.

bromine were at variance with our own observations, and a more rigorous proof of the identity of the two bodies was necessary. Fortunately a small amount (0.125 gram) of their old preparation still remained, and we were able to establish its identity with our own product, since it gave with aniline the same *α*-phenylamidocrotonolactone melting at 217°–218°,[1] and was attacked by bromine and water in the same way.

Action of Bromine.

α-Bromcrotonolactone is very slowly attacked by dry bromine at ordinary temperatures. If one molecule is added, the lactone does not dissolve at first, and the color of the bromine remains apparently unchanged for several days. The reaction then seems to proceed more rapidly, and at the end of the sixth day we found that the color had faded completely. The tube then opened with pressure, and a large amount of hydrobromic acid escaped. Substitution had evidently taken place, and the weight of the liquid product corresponded precisely with that which would theoretically be required by the replacement of one hydrogen atom by bromine. The product of the reaction remained for a long time liquid, and its alcoholic solution gave but a greenish color on the addition of sodic carbonate. After long standing in desiccator a few large clear crystals appeared, which from their melting-point (90°–91°) and other characteristics were shown to be the *αβ*-dibromcrotonolactone. After distilling with steam, in order to remove the dibromcrotonolactone, the aqueous solution left on evaporation a viscous residue. After long standing in a desiccator a few microscopic rhombic plates appeared, which were doubtless mucobromic acid. On repeating this experiment later, when the mean temperature of the room was much higher, the reaction was completed in about half the time; the product gave a decided blue color in alcoholic solution with sodic carbonate, showing the formation of mucobromyl bromide, but on long standing crystals of dibromcrotonolactone were also formed. On heating with two molecules of bromine for several hours at 100°, mucobromyl bromide is formed in quantity. The product gradually solidified on standing, gave an intense blue color with sodic carbonate, and after recrystallization from alcohol melted at 56°–57°.

[1] See page 282.

Action of Oxidizing Agents.

Concentrated nitric acid oxidizes the *a*-bromcrotonolactone without much difficulty at 100°. Carbonic dioxide is freely evolved, and a small quantity of a volatile oil is formed, which has a suffocating, sharp odor, and contains both nitrogen and bromine. We were unable to isolate other characteristic products of the reaction. With bromine in aqueous solution we had somewhat better success. The reaction progressed slowly, but after boiling for several hours with an excess of bromine a small amount of an oily product had been formed which was not further examined. The aqueous solution upon evaporation gave characteristic crystals of mucobromic acid, which, after recrystallization from water, melted at 120°–121°. The weight of mucobromic acid thus obtained was, however, barely 20 per cent. of the theoretical amount, and carbonic dioxide was also formed in the reaction. Hill and Sanger had found that the body which they described as having the composition of a bromcrotonolactone and melting at 77°, was converted by bromine and water into an amorphous substance insoluble or sparingly soluble in all common solvents. Two experiments which we tried with small quantities of their old preparation failed to confirm their statements. It gave precisely the same results which we had already obtained with the *a*-bromcrotonolactone. The yield of mucobromic acid given by the reaction is so small, and the quantity of the old material at our disposal was so limited, that we were unable to purify our product sufficiently for a sharp determination of the melting-point. Its appearance and behavior left no doubt as to its identity.

Action of Aniline.

If aniline is added to a solution of the *a*-bromcrotonolactone in dilute alcohol, the bromine is gradually displaced at ordinary temperatures, and the corresponding phenylamidocrotonolactone is formed. The somewhat dark-colored crystalline mass, which separates after the lapse of twenty-four hours, may be purified by recrystallization from glacial acetic acid, and afterward from alcohol. The *a*-chlorlactone which was described by Hill and L. L. Jackson,[1] and of which we shall speak later, also reacts as readily with aniline, and naturally gives the same product. The

[1] Proc. Am. Acad. **24**, 353.

same body may furthermore be made, although with more difficulty, by the reduction of the α-phenylamido-β-bromcrotonolactone. The elimination of the bromine takes place so slowly in acid solution that we have found it more advantageous to employ sodium amalgam with dilute alcohol, and to allow the reduction to proceed in alkaline solution at ordinary temperatures. Although more or less decomposition of the phenylamidobromcrotonolactone takes place, as the strong odor of phenyl isocyanide which is developed shows, a satisfactory product is obtained in this way. The finely powdered α-phenylamido-β-bromcrotonolactone is suspended in 50 times its weight of about 60-per cent. alcohol, and an excess of sodium amalgam containing 2 per cent. of metallic sodium is added. The substituted lactone gradually goes into solution, and we usually have found the reduction complete at the end of four or five hours. The clear solution is then acidified with acetic acid, the alcohol driven off upon the water-bath, and the crystalline product which separates recrystallized from glacial acetic acid. Occasionally we have found it necessary to treat the product a second time with sodium amalgam in order to remove the last traces of bromine.

I. 0.1991 gram substance gave 0.4996 gram CO_2 and 0.0962 gram H_2O.

II. 0.2114 gram substance gave 14.9 cc. of moist nitrogen at 21.3° and under a pressure of 754 mm.

	Calculated for $C_{10}H_9NO_2$.	Found. I.	II
C	68.57	68.42	...
H	5.14	5.36	...
N	8.00	...	7.94

α-Phenylamidocrotonolactone is very sparingly soluble even in boiling water. It dissolves quite readily in boiling alcohol, more sparingly in cold, and very sparingly in hot benzol or chloroform; in ether, ligroïn, or carbonic disulphide, it is nearly insoluble. It is readily soluble in hot glacial acetic acid, and crystallizes on cooling in feather-formed aggregations of branching needles. The melting-point of the substance varies somewhat according to the rapidity with which it is heated; but with proper care to avoid long heating it was found to melt quite sharply at 217°–218°, although decomposition ensued on further heating. Material made from the α-chlor- and α-bromlactones, as well as by the

reduction of the phenylamidobromlactone, showed identically the same behavior on heating, and when tested side by side in the same bath melted at the same temperature. The body dissolves readily in hot concentrated hydrochloric acid, but aniline seems to be formed at once. In hot alkaline solutions it dissolves somewhat more readily than in water, and if such a hot solution is quickly cooled it separates apparently unchanged. On longer heating decomposition sets in. A solution of the body in hot dilute baric hydrate was boiled for a short time and distilled. The distillate contained aniline in abundance, as was shown by the formation of tribromaniline melting at 118°–119°. At the same time baric carbonate had been precipitated, and in solution was found a barium salt which was extremely soluble in water, was precipitated by alcohol from the concentrated aqueous solution in an amorphous form, and was left as a brownish varnish upon evaporation.

Reduction of the $\alpha\beta$-Dibromcrotonolactone to Crotonolactone.

When dibromcrotonolactone is heated to 100° with dilute sulphuric acid and granulated zinc it is rapidly reduced, and at the end of several hours the reduction is complete. It was easy to prove by quantitative determinations that all the bromine of the original substance had been converted into hydrobromic acid, and the behavior of the solution toward decinormal potassic hydrate also showed that it contained a lactone in nearly theoretical quantity. We found it practically impossible to extract the lactone from aqueous solution, and we therefore distilled this solution in a current of steam. The distillate which we obtained was feebly acid, but it also contained a small quantity of a lactone, which, however, we found by titration to be relatively large in proportion to the free acid. The amount of free acid varied very much in our preparations, and apparently disappeared entirely, if during the reduction too large an excess of sulphuric acid was not used. With ordinary care the free acid did not correspond to as much as one-tenth of the total alkali which was neutralized on boiling, and we were unable to increase that amount beyond one-fifth by any modification of the mode of reduction. Our determinations furthermore showed that each litre of distillate could contain but 1.25 grams of crotonolactone if this body had

really been formed by reduction. We made many fruitless attempts to isolate the crotonolactone from this dilute aqueous solution, and since our main object was to establish beyond question the lactone-nature of the dibromcrotonolactone from which it had been formed, we proceeded at last to prepare from the solution a salt of the corresponding oxycrotonic acid. To the dilute lactone solution we add slightly more than the required amount of baric hydrate, heated the alkaline solution to boiling, precipitated after the lapse of some time the slight excess of baric hydrate by carbonic dioxide, and evaporated to small volume the filtered solution. We obtained in this way a somewhat brown syrupy residue, which on drying yielded a hard varnish. For its purification is was dissolved in a small amount of water, and alcohol added until a portion of the salt had been precipitated. The filtered solution was then concentrated by evaporation, a trace of a haloid barium salt removed by the cautious addition of argentic carbonate, and the clear solution evaporated upon the water-bath. After drying for some time at 100°, the gummy salt became sufficiently friable to enable us to powder it, and it was then thoroughly dried at 100°. A complete analysis showed that this salt had the composition of a baric oxycrotonate. The second determination of carbon was made in the wet way by the method of Messinger,[1] the first by the more usual method with potassic dichromate in the open tube.

I. 0.1961 gram salt gave 0.2044 gram CO_2 and 0.0694 gram H_2O.

II. 0.1432 gram salt gave 0.1503 gram CO_2.

III. 0.2414 gram salt gave 0.1655 gram $BaSO_4$.

	Calculated for $Ba(C_4H_3O_3)_2$.	Found. I.	II.	III.
C	28.30	28.42	28.63	...
H	2.95	3.93	...	...
Ba	40.44	...	...	40.33

The formation of the crotonolactone through the reduction of the dibromcrotonolactone was thus established. Since the salts of the oxycrotonic acid all seemed to possess the same uninviting properties, and our main end was already reached, we made no further study of them.

[1] Ber. d. chem. Ges. **21**, 2910.

$\alpha\beta$-DICHLORCROTONOLACTONE.

The $\alpha\beta$-dichlorcrotonolactone may be prepared most easily by the reduction of mucochloryl bromide. This body, which has not yet been described, was readily made by the action of phosphorous tribromide upon mucochloric acid. The reaction ran perfectly smoothly, and but little more than one molecule of phosphorous tribromide was needed for complete reaction with three molecules of mucochloric acid. After heating at 100° until the liquefied product grew turbid with the separation of phosphorous acid, the flask was well cooled, and cold water added with constant shaking. The oil which separated gradually solidified, and the granular product which was obtained could readily be collected by filtration. As in the preparation of mucobromyl bromide, we have found it easy to obtain 88–90 per cent. of the theoretical yield, and the crude product was sufficiently pure for further use. An analysis of a sample recrystallized from ligroïn gave the required percentage of halogen.

0.2721 gram substance gave 0.5556 gram AgCl + AgBr.

	Calculated for $C_4HCl_3O_2Br$.	Found.
Cl + Br	65.09	64.91

Mucochloryl bromide is very readily soluble in alcohol, ether, chloroform, carbonic disulphide or benzol; in ligroïn it is somewhat more sparingly soluble. From a solution in dilute alcohol it may be obtained by spontaneous evaporation in large transparent plates which melt at 36°. In alcoholic solution it gives with dilute alkalies a deep purple color, which rapidly passes into a wine-red and finally to yellow. With sodic carbonate we have also frequently noticed the formation of a deep green color after the wine-red.

The reduction of the mucochloryl bromide is easily effected by means of stannous chloride and hydrochloric acid. The reaction proceeds slowly in the cold, but may be carried to the end at ordinary temperatures. On warming gently it runs rapidly with the evolution of heat, and in a short time, if the reaction is promoted by vigorous shaking, the mucochloryl bromide completely disappears. On cooling and adding water the dichlorlactone separates in long slender needles, while the mother-liquor yields on distillation with steam a small quantity of the same body. The yield amounts to 78 per cent. of the weight which could theoretically be

obtained from the mucochloryl bromide, or taking both reactions into account, 70 per cent. of the amount which the mucochloric acid employed should give. The substance recrystallized from ligroïn gave on analysis the following results:

I. 0.4362 gram substance gave 0.4955 gram CO_2 and 0.0574 gram H_2O.

II. 0.3097 gram substance gave 0.5789 gram AgCl.

	Calculated for $C_4H_2Cl_2O_2$.	Found. I.	II.
C	31.37	30.97	...
H	1.31	1.46	...
Cl	46.40	...	46.21

This dichlorcrotonolactone we have also made by the decomposition of trichlorpyromucic acid, and by the action of bromine-water upon $\beta\gamma$-dichlorpyromucic acid. Trichlorpyromucic acid appears to be more stable than tribrompyromucic acid. Still it is slowly decomposed with the evolution of carbonic dioxide, when heated to boiling with 50-per cent. sulphuric acid, and the dichlorlactone is formed. We have made by this method only a sufficient quantity of material to enable us to identify it with precision. In studying the action of bromine upon $\beta\gamma$-dichlorpyromucic acid we followed the same method that we had employed with the $\beta\gamma$-dibrompyromucic acid, and found that the reaction followed precisely the same course. In this case, however, we proved the presence of mucochloryl bromide among the insoluble products of the reaction only through the characteristic color which was developed upon the addition of sodic carbonate to the alcoholic solution. The dichlorlactone was isolated from the aqueous solution by distillation with steam, as well as by extraction with ether. Its identity was proved by its melting-point, and by its conversion into α-phenylamido-β-chlorcrotonolactone melting at 183°.[1]

$\alpha\beta$-Dichlorcrotonolactone is very readily soluble in benzol or chloroform, readily in alcohol or ether, somewhat more sparingly soluble in carbonic disulphide, and sparingly soluble in cold ligroïn, although more freely soluble in hot. It dissolves quite readily in boiling water, and volatilizes freely with steam. The substance crystallizes ordinarily in long silky needles, but on slow evaporation of the ethereal solution it is deposited in clear six-sided plates. It melts at 50°–51°, and boils under a pressure of

[1] See page 288.

18 mm. at 114°–115° without noticeable decomposition. With aqueous alkalies it behaves like the corresponding bromine compound, and gives a bright yellow solution. Hydroxylamine has no action upon it, and phenylhydrazine removes chlorine without forming any crystalline product. Aniline when added to its solution in dilute alcohol gives the highly crystalline α-phenylamido-β-chlorcrotonolactone. Hydriodic acid gives at 100° the α-iodo-β-chlorcrotonolactone.

Action of Oxidizing Agents.

αβ-Dichlorcrotonolactone is oxidized with even more difficulty than the corresponding dibromlactone. After boiling for several hours with eight times its weight of concentrated nitric acid (sp. gr. 1.42), a large part of the lactone remained unaltered, and could be recovered by distillation with steam. The aqueous solution was then evaporated to dryness on the water-bath, and the crystalline residue treated with small quantities of cold water. Mucochloric acid was then left behind, which after recrystallization from hot water melted at 124°–125°. The cold water had taken up a small quantity of a readily soluble acid, which undoubtedly was dichlormaleic acid. Since mucochloric acid yields dichlormaleic acid on oxidation with nitric acid, although it is attacked with more difficulty than mucobromic acid, it did not seem to us worth while to take further steps for its preparation in larger quantity and identification. Bromine dissolved in concentrated hydrochloric acid oxidizes the dichlorlactone, although in this case also long-continued boiling is required to complete the reaction.

Action of Aniline.

Aniline readily reacts upon the αβ-dichlorcrotonolactone at ordinary temperatures, and forms the α-phenylamido-β-chlorcrotonolactone. The reaction runs best with a dilute solution in 50-per cent. alcohol, and on standing the product separates in broad glistening leaflets, which are more or less highly colored. This color may be removed by recrystallization from glacial acetic acid or from alcohol.

0.1491 gram substance gave 0.1011 gram AgCl.

	Calculated for $C_{10}H_8ClNO_3$.	Found.
Cl	16.91	16.76

α-Phenylamido-β-chlorcrotonolactone is quite readily soluble in boiling alcohol, and but sparingly soluble in cold. It also dissolves quite freely in boiling chloroform or benzol, more sparingly in ether or carbonic disulphide, and is almost insoluble in ligroïn. It is very sparingly soluble in boiling water, and is deposited in the form of fine needles as the solution cools. From chloroform it crystallizes in clear flat prisms, which melt quite sharply at 183°, although decomposition sets in at a somewhat higher temperature. Toward alkalies it behaves like the corresponding bromine derivative. It dissolves more freely in dilute sodic hydrate on heating than in water, and, if this solution is quickly cooled, it crystallizes out apparently unchanged. On longer heating decomposition ensues with the formation of phenyl isocyanide.

Action of Hydriodic Acid.

The action of hydriodic acid upon the αβ-dichlorcrotonolactone we have studied only so far as to prove that α-iodo-β-chlorcrotonolactone is formed. This body we have also made directly from mucochloryl bromide by the action of hydriodic acid at 100°. In order to keep up the strength of the hydriodic acid we found it advantageous to add at the same time potassic iodide and red phosphorus. The product was precipitated by the addition of water, decolorized with sulphurous acid, and recrystallized from alcohol.

0.2015 gram substance gave 0.3116 gram AgCl + AgI.

	Calculated for $C_4H_3ClIO_2$.	Found.
Cl + I	66.45	66.36

α-Iodo-β-chlorcrotonolactone dissolves very readily in benzol, is freely soluble in ether, but is more sparingly soluble in chloroform or carbonic disulphide. It dissolves easily in hot alcohol, but as this solution cools the greater part separates in long flattened needles which melt at 108°–109°. In its behavior toward reagents it closely resembles the bodies of similar constitution already described.

β-Chlorcrotonolactone.

By the action of zinc-dust and glacial acetic acid the αβ-dichlorcrotonolactone may be reduced without difficulty to the β-chlorcrotonolactone, but the physical properties of the latter body make its isolation a little more troublesome than that of the correspond-

ing body containing bromine. We dissolved the dichlorcrotonolactone in nearly twice its weight of 80-per cent. acetic acid, and slowly added, with cooling, somewhat more than the theoretical quantity of zinc-dust. The reduction was at first attended with the evolution of heat, but afterward became sluggish. After standing over night, the viscous solution, in which some metallic zinc was still suspended, was warmed, filtered, and the clear filtrate diluted with water. As the oil which was then precipitated showed no tendency to crystallize when cooled and scratched, the whole was extracted with ether, the ethereal solution washed with a dilute solution of sodic carbonate, dried with calcic chloride, and the ether removed by distillation. The liquid residue left by the ether was then distilled under diminished pressure. After two distillations the greater part of the product was collected between 128° and 130°, under a pressure of 22 mm., and on cooling this fraction to 10° the larger portion of it solidified. The solid was drained on the pump in a Gooch crucible, and carefully pressed with filter-paper. This perfectly dry material was then melted, cooled, and the crystalline solid again pressed, and these operations repeated for a second time without raising the melting-point perceptibly. An analysis showed that the body was a chlorcrotonolactone.

0.3071 gram substance gave 0.3720 gram AgCl.

	Calculated for $C_4H_3ClO_2$.	Found.
Cl	29.95	29.95

The β-chlorcrotonolactone is very readily soluble in alcohol, ether, chloroform, or benzol; less soluble in carbonic disulphide, and sparingly soluble in ligroïn. It may be crystallized most conveniently by strongly cooling the ethereal solution after the addition of ligroïn. It crystallizes in well-formed flat prisms, which melt at 25°–26°. The boiling-point of the pure substance was found to be 124°–125° under a pressure of 18 mm. It is quite freely soluble in hot water, and distils slowly with steam. Toward the alkaline hydrates and aniline it behaves like the β-bromcrotonolactone. We have not yet studied its behavior toward bromine or oxidizing agents. Although the $\beta\delta$-dichlorpyromucic acid is an extremely expensive substance on account of the difficulties which lie in the way of its preparation, and the small yield which can be obtained, its conversion into this same β-chlorcrotonolactone by heating with acids seemed to us of suffi-

cient importance to warrant an experiment in this direction. We therefore heated to boiling 0.7 gram of the acid with 7 grams of sulphuric acid of sp. gr. 1.43. Carbonic dioxide was slowly evolved, and the sulphuric acid became strongly colored. After boiling for several hours the solution was cooled, diluted, and extracted with ether. The ethereal extract was then washed with a dilute solution of sodic carbonate, which took up a small amount of the unaltered dichlorpyromucic acid; and dried with calcic chloride. The greater part of the ether was removed by distillation, the residue transferred to a weighing-tube and heated to 60°–80° *in vacuo*. The liquid residue which remained weighed 0.13 gram, and on cooling to 13° it almost completely solidified. The well-pressed crystalline solid remained friable at the temperature of the room (20°) and melted at 25°–26°. Recrystallization from a mixture of ether and ligroïn failed to raise this melting-point. It was thus proved that the β-chlorcrotonolactone had been formed by the decomposition of the $\beta\delta$-dichlorpyromucic acid.

α-Chlorcrotonolactone.

The α-chlorcrotonolactone melting at 52°–53° was prepared several years ago by Hill and L. L. Jackson[1] through the decomposition of the $\gamma\delta(\chi)$-dichlorpyromucic acid. The close relationship between this substance and a body of similar composition containing bromine, which had been discovered by Hill and Sanger,[2] was recognized at the time, but no attempt was made to establish experimentally this connection. The body containing bromine, which was described by Hill and Sanger, has already been shown to be the α-bromcrotonolactone, and it is easy to establish the identity in structure of the bromine and chlorine derivatives through the reaction with aniline. The α-chlorcrotonolactone when dissolved in dilute alcohol yields with aniline the α-phenylamidocrotonolactone melting at 217°–218°, which we have already described as prepared in the same way from the α-bromcrotonolactone.

Since the α-bromcrotonolactone had been made from the $\beta\delta$-dibrompyromucic acid through the reduction of the brom-maleyl bromide, which is formed from it by the action of bromine, it seemed to us of interest to prepare the α-chlorcrotonolactone by the same method from the $\beta\delta$-dichlorpyromucic acid. Pure

[1] Proc. Am. Acad. **24**, 353. [2] *Ibid.* **21**, 158.

$\beta\delta$-dichlorpyromucic acid was suspended in 25 times its weight of cold water, and dissolved by the cautious addition of sodic carbonate. Two molecules of bromine were then added to the feebly alkaline solution, and the whole allowed to stand over night. As the oil which had separated would not crystallize when strongly cooled and scratched, it was taken up with ether, and the residue left on the evaporation of the ether dissolved in 80-per cent. acetic acid. Zinc-dust was then added to this solution with careful cooling. When the reaction appeared to be complete, the filtered solution was diluted, extracted with ether, the ethereal solution washed with sodic carbonate and distilled. The residue soon crystallized in long slender prisms, which when recrystallized from ligroïn melted at 52°–53°, and in other respects showed the behavior of the α-chlorcrotonolactone. The $\beta\delta$-dichlorpyromucic acid, like the corresponding acid containing bromine, may, therefore, be made to yield either the α- or the β-chlorcrotonolactone. While we had no doubt that the $\gamma\delta$-dichlorpyromucic acid would show an essentially different behavior, and would yield, when treated in this way, the same α-chlorcrotonolactone which it gives when heated with acids, we thought it worth while to establish the fact by experiment. The $\gamma\delta$ dichlorpyromucic acid was therefore treated with bromine in a feebly alkaline solution, and the oil, which was thus formed, was then reduced with zinc-dust and glacial acetic acid. It was easy to isolate, as before, the α-chlorcrotonolactone melting at 52°–53° with its characteristic properties.

α-Phenoxy-β-bromcrotonolactone.

Many years ago Hill and Stevens[1] prepared from mucobromic acid, by the action of potassic phenylate, a derivative of mucobromic acid, in which one atom of bromine was replaced by the phenoxy group, and to which they gave the name mucophenoxybromic acid.[2] They showed that this acid had the same general structure as the mucobromic acid, in that it could be converted by oxidation into a phenoxybrommaleic acid, and that it yielded on

[1] Proc. Am. Acad. **19**, 262.

[2] Beilstein in the second edition of his "Handbuch der organischen Chemie" (II. 429) has seen fit to change this name to phenoxymucobromic acid. It is quite possible that we might have selected a better name for our new body, but it cetainly would be difficult to find one more misleading than that which Beilstein has chosen to give it. Whatever else it may be, it certainly is *not* a phenoxymucobromic acid. H. B. H.

decomposition with alkalies a phenoxybromacrylic acid. The stability of the latter acid in alkaline solution led them to the conclusion that it contained the phenoxy group in the α position. Although none of the substituted crotonolactones which we had studied could directly be converted into the salts of the oxy-acids, it seemed to us probable that the corresponding bodies containing the phenoxy group would react more smoothly. As the preliminary experiments which we made on the action of sodic or potassic phenylate upon the dibromcrotonolactone gave us little hope that the desired bodies could be made in this way, we turned to the mucophenoxybromic acid, and found that the α-phenoxy-β-bromcrotonolactone could easily be made by the reduction of its bromanhydride.

The mucophenoxybromyl bromide was not described by Hill and Stevens, but we found that it could be made without difficulty, in nearly theoretical quantity, by the action of phosphorous tribromide. We used but little more than one molecule of the tribromide to three molecules of the acid, and heated at 100°. When the liquid product became turbid with the separation of phosphorous acid, we added cold water with constant shaking. The bromide immediately separated in a granular form, and could be recrystallized from small quantities of alcohol. It formed fine concentrically grouped needles, which melted at 95°–96°.

0.2363 gram substance gave 0.2656 gram AgBr.

	Calculated for $C_4H(OC_6H_5)Br_2O_3$.	Found.
Br	47.90	47.82

Mucophenoxybromyl bromide is readily soluble in ether, chloroform, or benzol, readily soluble in hot alcohol, more sparingly in cold, and sparingly soluble in ligroïn. With alkalies in alcoholic solution it gives a yellow color. The reduction of this body to the corresponding lactone is slowly but completely effected by stannous chloride and hydrochloric acid at ordinary temperatures, if a little alcohol be added at the same time to facilitate solution. We have found it more convenient, however, to use zinc-dust and acetic acid. Since the lactone is almost insoluble in dilute acetic acid, and an excess of zinc-dust apparently does no harm, we suspended the bromide in twice its weight of glacial acetic acid (99.5-per cent.), and slowly added with careful cooling an excess of zinc-dust. After standing for several

hours, the reduction is complete, and the addition of water to the filtered solution throws down a beautifully crystalline substance, which may be recrystallized from alcohol. The product thus obtained proved on analysis to have the composition of a phenoxybromcrotonolactone. The weight of the lactone as precipitated by water was 80 per cent. of the theoretical amount.

I. 0.3929 gram substance gave 0.6796 gram CO_2 and 0.1008 gram H_2O.

II. 0.1906 gram substance gave 0.1410 gram AgBr.

	Calculated for $C_4H_3(OC_6H_5)BrO_2$.	Found. I.	II.
C	47.07	47.18	...
H	2.75	2.85	...
Br	31.37	...	31.48

The α-phenoxy-β-bromcrotonolactone is readily soluble in ether, chloroform, benzol, glacial acetic acid, or in hot alcohol, and but sparingly soluble in cold alcohol or in ligroïn. It dissolves slightly in boiling water, and volatilizes slowly with steam. In alcoholic solution it is not attacked by aniline at ordinary temperatures. With aqueous alkalies it is slowly carried into solution, on heating, with the formation of the corresponding salts of the oxy-acid.

α-Phenoxy-β-brom-γ-oxycrotonic Acid.—If the α-phenoxy-β-bromcrotonolactone is dissolved in a hot solution of potassic hydrate, and after thorough cooling a slight excess of hydrochloric acid is added, the solution soon becomes filled with colorless pearly scales of the phenoxybromoxycrotonic acid. For analysis the substance was merely washed well with cold water and dried over sulphuric acid.

I. 0.2782 gram substance gave 0.4484 gram CO_2 and 0.0857 gram H_2O.

II. 0.1588 gram substance gave 0.1092 gram AgBr.

	Calculated for $C_4H_4(OC_6H_5)BrO_2$.	Found. I.	II.
C	43.95	43.96	...
H	3.30	3.08	...
Br	29.30	...	29.25

The α-phenoxy-β-brom-γ-oxycrotonic acid is readily soluble in alcohol or ether, quite readily soluble in hot chloroform or benzol, and almost insoluble in ligroïn. From chloroform it crystallizes in brilliant flat rectangularly terminated prisms. It is very spar-

ingly soluble in cold water, and when warmed it dissolves somewhat more freely, but the solution immediately grows turbid with the formation of the still more sparingly soluble lactone. The identity of the phenoxybromcrotonolactone formed in this way was established by analysis.

0.2696 gram substance gave 0.2007 gram AgBr.

	Calculated for $C_4H_3(OC_6H_5)BrO_2$.	Found.
Br	31.37	31.66

The melting-point of the acid cannot be determined with precision, since it is converted into the lactone by heat, but under ordinary conditions it is found to be about 98°. The loss of weight which we observed on melting the acid by short exposure to a temperature of 110°, and allowing the fused mass to stand over sulphuric acid, corresponded to a little more than one molecule of water.

0.6318 gram substance lost 0.0450 gram H_2O.

	Calculated for $C_4H_4(OC_6H_5)BrO_3$.	Found.
H_2O	6.59	7.12

Baric α-Phenoxy-β-brom-γ-oxycrotonate, $Ba[C_4H_3(OC_6H_5)BrO_3]_2.3H_2O$.—The barium salt is readily soluble even in cold water, and crystallizes in flat prisms with rectangular terminations. It apparently contains three molecules of water, almost the whole of which it readily loses over sulphuric acid.

0.5891 gram air-dried salt lost over sulphuric acid 0.0430 gram H_2O, and at 100° it lost 0.0052 gram H_2O in addition.

	Calculated for $Ba[C_4H_3(OC_6H_5)BrO_3]_2.3H_2O$.	Found.
H_2O	7.35	8.18

0.4939 gram anhydrous salt gave 0.1677 gram $BaSO_4$.

	Calculated for $Ba[C_4H_3(OC_6H_5)BrO_3]_2$.	Found.
Ba	20.11	19.97

The anhydrous salt dissolves without difficulty in strong alcohol, but in a few moments the solution turns solid with the separation of finely felted needles of a salt containing alcohol of crystallization. The same salt may also be obtained by dissolving the hydrous salt in hot alcohol. We have been unable to obtain satisfactory determinations of the amount of alcohol which is thus taken up, since the salt effloresces very rapidly on exposure to the air, and loses the last part of its alcohol with great difficulty.

α-PHENOXY-β-CHLORCROTONOLACTONE.

It seemed to us desirable to confirm the results which we had obtained with the phenoxybromcrotonolactone by preparing also the corresponding bodies containing chlorine. Hill and Stevens had made no experiments as to the action of potassic phenylate upon mucochloric acid, but we found that mucophenoxychloric acid could readily be made in this way. As we were interested only in the preparation of the phenoxychlorcrotonolactone, Mr. H. P. Nash undertook a more careful study of this acid, and will present his results in a separate paper. From the mucophenoxychloric acid we prepared without difficulty the corresponding bromanhydride by the action of phosphorous tribromide. The reaction ran smoothly, and gave us, as in the previous cases, which we have described more in detail, about 90 per cent. of the theoretical yield. The body was readily soluble in ether, chloroform, benzol, or glacial acetic acid. It was very readily soluble in hot alcohol, more sparingly in cold; very sparingly soluble in cold ligroïn, though more easily soluble in hot. When recrystallized from small quantities of alcohol or from ligroïn, it was obtained in radiating needles which melted at 89°–90°.

0.2320 gram substance gave 0.2631 gram AgCl + AgBr.

	Calculated for $C_4H(OC_6H_5)ClO_2Br$.	Found.
Cl + Br	39.89	39.53

In the reduction of the mucophenoxychloryl bromide to the corresponding lactone we followed the method which had already proved convenient with the mucophenoxybromyl bromide. Zinc-dust was slowly added with careful cooling to the bromide dissolved in glacial acetic acid. When the reduction was complete the filtered solution was diluted with water, and the crystalline body which was thus thrown down was recrystallized from a small amount of alcohol. The lactone which was precipitated by water amounted to 76 per cent. of the theoretical yield.

I. 0.3243 gram substance gave 0.6765 gram CO_2 and 0.0995 gram H_2O.

II. 0.2256 gram substance gave 0.1541 gram AgCl.

	Calculated for $C_4H_2(OC_6H_5)ClO_2$.	Found. I.	Found. II.
C	57.02	56.89	...
H	3.33	3.40	...
Cl	16.87	...	16.89

The α-phenoxy-β-chlorcrotonolactone is readily soluble in ether, chloroform, benzol, carbonic disulphide, and in hot alcohol or ligroïn, although but sparingly soluble in these solvents when cold, and almost insoluble in water. From alcohol it crystallizes in six-sided plates, or flattened prisms, which melt at 67°–68°. In alcoholic solution it is not affected by aniline at ordinary temperatures. When heated with aqueous alkalies it is gradually carried into solution with the formation of the salt of the corresponding oxy-acid.

α-Phenoxy-β-chlor-γ-oxycrotonic Acid, $C_4H_4(OC_6H_5)ClO_3$.—If the α-phenoxy-β-chlorcrotonolactone is dissolved in a moderately dilute solution of potassic hydrate by the aid of heat, and to the well-cooled solution a slight excess of hydrochloric acid is added, the phenoxychloroxycrotonic acid separates almost immediately in colorless pearly scales. The crystals were removed by filtration, thoroughly washed with cold water and dried over sulphuric acid. The substance was then analyzed without further purification.

I. 0.4291 gram substance gave 0.8242 gram CO_2 and 0.1541 gram H_2O.

II. 0.2160 gram substance gave 0.1342 gram AgCl.

	Calculated for $C_4H_4(OC_6H_5)ClO_3$.	Found. I.	II.
C	52.51	52.37	...
H	3.94	3.99	...
Cl	15.52	...	15.36

α-Phenoxy-β-chlor-γ-oxycrotonic acid crystallizes in flat rectangularly truncated prisms, which melt at about 76°, but the melting-point varies with the rapidity of the heating. It is very soluble in alcohol or ether, quite readily soluble in chloroform or benzol, less soluble in carbonic disulphide or ligroïn, and sparingly soluble in water. On heating with water it behaves like the compound containing bromine, which has already been described, and is rapidly converted into the lactone. This conversion is immediately effected when the acid is heated to its melting-point. The acid was melted by short exposure to a temperature of 110°, and the fused mass thoroughly dried over sulphuric acid. The loss in weight corresponded almost exactly to that required by one molecule of water.

0.4068 gram substance lost 0.0333 gram H_2O.

	Calculated for $C_4H_4(OC_6H_5)ClO_3$.	Found.
H_2O	7.88	8.11

The acid may also be converted into the lactone by longer continued heating at a temperature below its melting-point, and this change seems to take place slowly even at ordinary temperatures. After the lapse of many weeks a combustion of the material which had previously given us the proper percentage of chlorine showed that the acid had in part been converted into the lactone.

0.2004 gram substance gave 0.4018 gram CO_2 and 0.0676 gram H_2O.

	Calculated for $C_4H_4(OC_6H_5)ClO_2$.	Calculated fo $C_4H_3(OC_6H_5)C\,O_2$.	Found.
C	52.51	57.02	54.69
H	3.94	3.33	3.75

Baric α-Phenoxy-β-chlor-γ-oxycrotonate, $Ba[C_4H_3(OC_6H_5)ClO_2]_2.3H_2O$.—The barium salt of the acid is very soluble even in cold water, and crystallizes in long colorless prisms. The air-dried salt contains three molecules of water, all of which it loses over sulphuric acid.

0.5906 gram air-dried salt lost over sulphuric acid 0.0492 gram H_2O, and when heated at 100° it lost in addition 0.0002 gram H_2O.

	Calculated for $Ba[C_4H_3(OC_6H_5)ClO_2]_2.3H_2O$.	Found.
H_2O	8.36	8.36

0.4814 gram anhydrous salt gave 0.1869 gram $BaSO_4$.

	Calculated for $Ba[C_4H_3(OC_6H_5)ClO_2]_2$.	Found.
Ba	23.19	22.82

This salt behaves toward alcohol precisely like the baric phenoxybromoxycrotonate, and forms the same finely felted needles.

Mucobromic Acid.

It was shown many years ago by Hill and O. R. Jackson[1] that mucobromic acid could be converted into dibrommaleic acid by oxidation with argentic oxide. When their investigation was completed (1880), it was already known that phenylhydrazine reacted upon certain aldehydes, but experimental evidence as to the generality of the reaction had not accumulated, and the importance of this body as a reagent for aldehydes and ketones was not urged by E. Fischer[2] until several years later. The char-

[1] Proc. Am. Acad. **16**, 186. [2] Ber. d. chem. Ges. **17**, 572.

acteristic behavior of hydroxylamine with aldehydes and ketones was also not discovered by V. Meyer[1] until two years later. Since the facts which we have described in the preceding pages tended to show that mucobromic acid was an oxylactone and not an aldehyde acid, it was evidently necessary for us to study its behavior toward phenylhydrazine and hydroxylamine. Phenylhydrazine has unfortunately given us no bodies the physical properties of which invited further investigation, but with hydroxylamine we have been more successful. We have also studied the action of ammonia upon ethyl mucobromate, and found that mucobromamide is thus formed.

Mucobromoxime, $C_4H_3Br_2NO_3$.—Hydroxylamine acts with great ease upon mucobromic acid, but we have been able to isolate the oxime only when the reaction takes place in an alkaline aqueous solution. The decomposition is almost instantaneous, so that after the lapse of a few minutes the solution deposits upon acidification the oxime in a granular condition. This granular precipitate was at once removed by filtration, well washed with cold water and dried over sulphuric acid.

I. 0.2397 gram substance gave 0.1575 gram CO_2 and 0.0415 gram H_2O.

II. 0.3133 gram substance gave 0.2043 gram CO_2.[2]

III. 0.2524 gram substance gave 0.3481 gram AgBr.

	Calculated for $C_4H_3Br_2NO_3$.	Found. I.	II.	III.
C	17.58	17.92	17.58	...
H	1.10	1.92	...	...
Br	58.61	...	...	58.68

This oxime is readily soluble in alcohol or ether, and but sparingly soluble in chloroform or benzol. In cold water it is also sparingly soluble, but dissolves readily on boiling. If the hot solution is immediately cooled the oxime anhydride separates, but otherwise the acid ammonium salt of dibrommaleic acid is formed, and remains in solution. The oxime has no definite melting-point, but is evidently converted into the anhydride by heat. It usually melts, at least in part, at about 90°, but this point varies with the rate of heating.

Mucobromoxime Anhydride, $C_4HBr_2NO_3$.—Under ordinary

[1] Ber. d. chem. Ges. **15**, 1165, 1324, 1527, 2778, 2783; **16**, 822.

[2] The hydrogen in this combustion was lost.

conditions the only product formed by the action of hydroxylamine or its hydrochloride upon mucobromic acid is the anhydride of the oxime. Moreover, if in the preparation of the oxime by the method just described the precipitated substance is allowed to stand for several hours in the mother-liquor the anhydride is formed. The material used in Analysis III was made by the action of hydroxylamine hydrochloride upon a solution of mucobromic acid in strong methyl alcohol; for the other determinations, preparations were employed which had been made in a solution in dilute methyl alcohol with the addition of one equivalent of sodic carbonate. In each case the reaction ran rapidly at ordinary temperatures, and the anhydride which separated was washed well with cold water, and dried over sulphuric acid.

I. 0.2927 gram substance gave 0.4334 gram AgBr.

II. 0.2393 gram substance gave 0.3547 gram AgBr.

III. 0.1801 gram substance gave 0.2670 gram AgBr.

IV. 0.2014 gram substance gave 10.0 cc. of moist nitrogen at 19° and under a pressure of 753 mm.

V. 0.3127 gram substance gave 14.5 cc. of moist nitrogen at 15° and under a pressure of 764 mm.

	Calculated for $C_4HBr_2NO_2$.	Found. I.	II.	III.	IV.	V.
Br	62.75	63.00	63.07	63.08	...	...
N	5.49	...	...	...	5.65	5.45

Mucobromoxime anhydride dissolves quite readily in alcohol, chloroform, or benzol; with somewhat more difficulty in ether or carbonic disulphide; and is almost insoluble in ligroïn. It crystallizes in dendritic needles, which melt at about 117°–118°, but this melting-point varies with the conditions under which it is taken. If the melted substance be heated to a higher temperature, it solidifies again below 140° and melts then for a second time at 218°. This behavior is due to the conversion of the anhydride into the isomeric dibrommaleinimide, which melts, according to Ciamician and Silber,[1] at 225°. If this isomerization is brought about by plunging the tube containing a considerable quantity of the substance into a bath heated to 115°, the reaction is violent, but also attended with decomposition. The anhydride is sparingly soluble in cold water, although more readily in hot. If the hot solution is quickly cooled the anhydride separates, but on

[1] Ber. d. chem. Ges. **17**, 556.

prolonged heating it is completely converted into the acid ammonium salt of dibrommaleic acid. This acid was identified through its characteristic barium salt and the melting-point (114°) of its anhydride.

Methyl Ester of Mucobromoxime, $C_4H_2Br_2NO_2CH_3$.—Although hydroxylamine hydrochloride reacts at ordinary temperatures upon mucobromic acid when dissolved in strong methyl alcohol, and forms the mucobromoxime anhydride, if the reaction takes place at the boiling-point of the methyl alcohol the methyl ester of the oxime results. The same body is also formed when the anhydride is boiled for a short time with methyl alcohol. For its preparation we found it advantageous to dissolve mucobromic acid in rather less than twice its weight of methyl alcohol, to add a little more than one molecule of hydroxylamine hydrochloride dissolved in the smallest possible quantity of water, and to boil with reverse cooler for twenty minutes. On cooling, the methyl ester then separated in abundance.

I. 0.4336 gram substance gave 0.3370 gram CO_2 and 0.0915 gram H_2O.

II. 0.2946 gram substance gave 0.3899 gram AgBr.

	Calculated for $C_4H_3Br_2NO_3CH_3$.	Found. I.	Found. II.
C	20.90	21.19	...
H	1.74	2.34	...
Br	55.75	...	56.31

The methyl ester of mucobromoxime is readily soluble in alcohol, somewhat more sparingly soluble in ether, and very sparingly soluble in chloroform or benzol. It is also very sparingly soluble in cold water, but dissolves freely on heating, and, if the solution is quickly cooled, it separates in finely felted needles. On continued boiling it is converted into dibrommaleinimide, and the same change is also effected by longer boiling with methyl alcohol. The ester melts at 146°–147°, and at a slightly higher temperature solidifies with the formation of dibrommaleinimide, which again melts at 218°. The conversion of the ester into the imide may also be brought about by dissolving it in sodic carbonate, and acidifying the solution with hydrochloric acid. The imide melting at 218° is thus thrown down. If the alkaline hydrates are used to dissolve the ester, great care must be used to avoid an excess. The same ester may also be made

by the action of hydroxylamine hydrochloride upon methyl mucobromate dissolved in methyl alcohol. We found, however, that substantially no reaction took place when a 10-per cent. solution of the ester stood at ordinary temperatures for several days, either with free hydroxylamine or with its hydrochloride. The solutions when cooled with ice and salt deposited no crystals in material amount, and on dilution with water the original ester was recovered essentially unchanged. With free hydroxylamine there seemed to be but slow action even on boiling; but on boiling the solution containing the hydrochloride for half an hour, a copious separation of the methyl ester of the mucobromoxime melting at 146°–147° was obtained on cooling. On boiling for a longer time this ester was almost wholly converted into dibrommaleinimide melting at 218°.

Although it had been found that the methyl ester of mucobromoxime could not be dissolved in alkalies without the formation of dibrommaleinimide, it seemed to us possible that we might form a silver salt. On the addition of an alcoholic solution of argentic nitrate to an alcoholic solution of the ester, no salt was precipitated, and no crystals separated on standing. Alcoholic ammonia was then cautiously added, and the first drop brought down a heavy yellow pulverulent precipitate, although the addition of two molecules was necessary to complete the precipitation. The salt was insoluble in water or alcohol, and was not affected by an excess of ammonia. On analysis it proved to be an ammonio-silver salt of dibrommaleinimide, corresponding to the ammonio-silver compound of dichlormaleinimide described by Ciamician and Silber.[1] Nitric acid decomposed it with the liberation of dibrommaleinimide.

I. 0.2916 gram substance gave with HBr 0.1440 gram AgBr.

II. 0.2384 gram substance gave with HNO_3 and $AgNO_3$ 0.2347 gram AgBr.

III. 0.3502 gram substance gave 22.2 cc. of moist nitrogen at 19° and under a pressure of 754 mm.

	Calculated for $C_4Br_2NO_2AgNH_2$.	Found. I.	II.	III.
Ag	28.51	28.37	...	...
Br	42.23	...	41.89	...
N	7.39	...	...	7.37

[1] Ber. d. chem. Ges. **16**, 2394.

A salt which closely resembles that which we have just described is precipitated when an alcoholic solution of argentic nitrate is added to an alcoholic solution of dibrommaleinimide. It can contain no ammonia, however, and is the silver salt of the imide.

0.3153 gram substance gave 10.7 cc. of moist nitrogen at 17° and under a pressure of 777 mm.

	Calculated for $C_4Br_2NO_2Ag$.	Found.
N	3.87	4.02

The strongly acid filtrate from this salt gave with alcoholic ammonia an ammonio-silver salt identical with that prepared from the methyl ester of mucobromoxime.

0.3553 gram substance gave 21.9 cc. of moist nitrogen at 17° and under a pressure of 775 mm.

	Calculated for $C_4Br_2NO_2AgNH_3$.	Found.
N	7.39	7.30

In the preparation of the mucobromoxime methyl ester directly from mucobromic acid, there is also formed an oil, which, although somewhat soluble in water, is precipitated by the addition of water to the methyl-alcoholic mother-liquors. We have not obtained it in a condition fit for analysis, but as it is readily decomposed by water with the formation of dibrommaleic acid it is doubtless an acid ester of this acid.

Mucobromamide, $C_4HBr_2O_2NH_2$.—When ammonia gas is passed into a solution of ethyl mucobromate in dry ether, reaction immediately takes place, and mucobromamide separates. This body may also be prepared by the action of alcoholic ammonia upon an alcoholic solution of the ester at ordinary temperatures, but the product so obtained is dark-colored and must be treated with bone-black in acid solution, and recrystallized from hot water. We have also prepared mucobromamide by the action of ammonia upon mucobromyl bromide dissolved in anhydrous ether.

I. 0.3496 gram substance gave 0.2426 gram CO_2 and 0.0555 gram H_2O.

II. 0.3640 gram substance gave 0.5342 gram AgBr.

III. 0.2033 gram substance gave 10.7 cc. of moist nitrogen at 18.5°, and under a pressure of 769 mm.

	Calculated for $C_4HBrO_2NH_2$.	Found. I.	II.	III.
C	18.68	18.92	...	...
H	1.20	1.77	...	...
Br	62.26	...	62.44	...
N	5.45	...	...	6.13

Mucobromamide is nearly insoluble in ether, chloroform, or benzol, and is readily soluble in hot, more sparingly in cold alcohol. It dissolves very readily in hot water, and separates almost completely as the solution cools in colorless dendritic needles, which melt with decomposition at about 170°. Slight impurities apparently lower very greatly this point of melting and decomposition. Alkaline hydrates added in excess carry it completely into solution in the cold without the formation of any color, but, if an excess be not added, the solution rapidly turns brown or black. From the colorless solution the immediate addition of acid reprecipitates the amide unchanged. It may be recrystallized from hot concentrated hydrochloric acid, or from dilute sulphuric acid, but after long heating with concentrated hydrochloric acid, or boiling for a shorter time with distillable hydrobromic acid, mucobromic acid melting at 120° is formed. The amide dissolved readily in fuming nitric acid, and on long standing this solution deposited well formed crystals of dibrommaleinimide melting at 218°. Dilute solutions of chromic acid with an excess of sulphuric acid effected little change even on long boiling, but in concentrated solution oxidation took place and dibrommaleinimide was formed. This same body was also formed when the amide was heated with dry bromine at 100°.

We made many attempts to make from the mucobromamide by the action of hydroxylamine, phenylhydrazine, or aniline, the corresponding derivatives, but in no case were we successful. Either the amide was recovered unchanged or, in a few cases, in working with the free bases at higher temperatures a deeper decomposition ensued.

Mucochloric Acid.

Toward hydroxylamine mucochloric acid behaves in essentially the same way as mucobromic acid, although we have been unable as yet to prepare the anhydride of the oxime, the body which was most readily formed from mucobromic acid. The methyl ester of

mucochloric acid when treated with ammonia gave mucochloramide without difficulty.

Mucochloroxime, $C_4H_3Cl_2NO_3.\frac{1}{2}H_2O$.—Mucochloric acid was dissolved in a small amount of methyl alcohol, and one equivalent each of hydroxylamine and sodic carbonate dissolved in a little water were added. After the lapse of a few minutes the solution was acidified with hydrochloric acid and the oxime immediately separated. Analyses of the air-dried material (III) or of the substance dried over sulphuric acid (I and II) showed that in each case one half-molecule of water was retained. Since dichlormaleinimide was quickly formed at temperatures below 100°, no attempt was made to dehydrate the substance by heat.

I. 0.2220 gram substance gave 0.2014 gram CO_2 and 0.0471 gram H_2O.

II. 0.2008 gram substance gave 0.2992 gram AgCl.

III. 0.1927 gram substance gave 0.2851 gram AgCl.

	Calculated for $C_4H_3Cl_2NO_3.\frac{1}{2}H_2O$.	Found. I.	II.	III.
C	24.87	24.79	...	...
H	2.07	2.36	...	...
Cl	36.79	...	36.58	36.85

Mucochloroxime crystallizes in slender felted needles, which are readily soluble in alcohol or ether, and but sparingly soluble in cold water. It dissolves readily in hot water, and if the solution is quickly cooled, it separates apparently unchanged, but on heating for a short time with water it is converted into the acid ammonium salt of dichlormaleic acid. The identity of the acid extracted by ether from the acidified solution was established by the melting-point of its anhydride (119°). The melting-point of the oxime cannot be determined with precision, but it lies in the neighborhood of 90°. The melted oxime passes into the dichlormaleinimide which solidifies and again melts at 175°–177°.

Methyl Ester of Mucochloroxime, $C_4H_2Cl_2NO_3CH_3$.—The methyl ester of mucochloroxime is formed when a cold solution of the oxime in methyl alcohol is allowed to stand for twenty-four hours, or when mucochloric acid is dissolved in its own weight of methyl alcohol, hydroxylamine hydrochloride dissolved in a little water added in somewhat more than equivalent quantity, and the whole allowed to stand at ordinary temperatures. If the solution is boiled even for a short time the chief product is dichlormaleinimide.

The ester may also be made by the action of hydroxylamine hydrochloride upon methyl mucochlorate, provided the solution in methyl alcohol be allowed to stand for several days.

0.1676 gram substance gave 0.2437 gram AgCl.

	Calculated for $C_4H_3Cl_2NO_3CH_3$.	Found.
Cl	35.86	35.94

The methyl ester of the mucochloroxime crystallizes in flattened needles, the melting-point of which varies with the mode of heating. When introduced into a heated bath the substance melts promptly when the temperature is held at 135°. At higher temperatures the melted ester again solidifies, with the formation of dichlormaleinimide, which in its turn melts at 173°–174°. The ester is readily soluble in alcohol, ether, or chloroform, and but sparingly soluble in benzol or carbonic disulphide. It is also sparingly soluble in cold water, but dissolves more readily in hot water, and, if the solution is quickly cooled, it separates in long felted needles. On longer heating with water it is converted into dichlormaleinimide. The ester may also be converted into the imide by dissolving it in a solution of sodic carbonate, and acidifying with hydrochloric acid,—provided the solution is cold, and moderately concentrated, and the acid is immediately added.

Mucochloramide, $C_4HCl_2O_2NH_2$.—Mucochloramide is readily formed when ammonia gas is passed into a solution of methylmucochlorate in dry ether. The hard dark-colored mass which separates is ground up in a mortar with small quantities of cold water. The greater part of the coloring matter is thus removed, and the residue may then be recrystallized from boiling water.

0.2115 gram substance gave 0.3606 gram AgCl.

	Calculated for $C_4HCl_2O_2NH_2$.	Found.
Cl	42.27	42.15

Mucochloramide is readily soluble in alcohol, sparingly soluble in ether, and almost insoluble in chloroform. It dissolves readily in hot water, and as the solution cools the greater part is deposited in the form of small oblique prisms, which melt at about 166°. Like mucobromamide it dissolves readily in solutions of the alkaline hydrates, and is reprecipitated unchanged if the alkaline solution is immediately acidified. On boiling for some time with concentrated hydrochloric acid it is converted into mucochloric acid, as was shown by the melting-point, 124°.

Mucophenoxybromic Acid.

Mucophenoxybromoxime, $C_4H_3(OC_4H_5)BrNO_3$.—We have found that hydroxylamine readily reacts upon mucophenoxybromic acid, and that the corresponding oxime is formed both in alkaline and acid solution. It may conveniently be prepared by adding to a solution of the acid in 20 times its weight of 50-per cent. methyl alcohol the equivalent amount of hydroxylamine hydrochloride. After standing for a short time at ordinary temperatures the oxime begins to separate in beautiful clusters of long needles, and in a few hours the reaction is completed.

0.2717 gram substance gave 0.1791 gram AgBr.

	Calculated for $C_4H_3(OC_4H_5)BrNO_3$.	Found.
Br	27.97	28.04

Mucophenoxybromoxime is readily soluble in alcohol or ether, and insoluble in chloroform or benzol. It is almost insoluble in cold water, dissolves but sparingly in boiling, and separates apparently unchanged if the solution is quickly cooled. On long boiling it is decomposed, and the solution then contains ammonia and phenoxybrommaleic acid. The solution was acidified with hydrochloric acid, extracted with ether, and the acid removed from the ethereal solution with sodic carbonate. The alkaline solution then gave on acidification small clustered needles, which melted at 104°–105° when rapidly heated. On sublimation a crystalline body was obtained which melted at 91°. According to Hill and Stevens, phenoxybrommaleic acid, when quickly heated, melts at 104°–105°, and we found that their acid when sublimed yielded the anhydride melting at 91°. The oxime shows great variation in melting-point (120°–135°), according to the mode of heating, and we have not yet been able to show that it is converted into the phenoxybrommaleinimide by heat. The melted body did not solidify on further heating, nor did it crystallize on cooling.

Mucophenoxychloric Acid.

Mucophenoxychloroxime, $C_4H_3(OC_4H_5)ClNO_3$.—This body is formed by the action of either hydroxylamine, or its hydrochloride, at ordinary temperatures upon mucophenoxychloric acid. As in previous cases we used diluted methyl alcohol as a solvent. The oxime began to crystallize almost immediately, and the separation was in a short time complete. The material used in Analysis I

was prepared by the action of the free base; that in Analysis II with the hydrochloride.

I. 0.2025 gram substance gave 0.1202 gram AgCl.

II. 0.2137 gram substance gave 0.1294 gram AgCl.

	Calculated for $C_4H_3(OC_4H_3)ClNO_3$.	Found. I.	II.
Cl	14.70	14.68	14.97

Mucophenoxychloroxime crystallizes in clustered needles which melt at 112°-125°, according to the mode of heating. It dissolves readily in alcohol or ether, but is insoluble in chloroform or benzol. It is almost insoluble in cold water, dissolves somewhat more freely on heating, and crystallizes out unchanged if the solution is quickly cooled. On longer boiling it is decomposed, and the solution then contains the acid ammonium salt of an acid which we have not yet further examined.

Contributions from the Chemical Laboratory of the Rose Polytechnic Institute.

IX.—CAMPHORIC ACID.

By W. A. Noyes.

The great variety of formulæ which have been proposed for camphor and for camphoric acid indicates that there is, as yet, no general agreement among chemists as to the structure of these bodies. The experiments described below were undertaken in the hope of obtaining derivatives of camphoric acid which would throw new light upon the question. While the work has not yet progressed far enough to aid essentially in the determination of structure, the fact that many chemists are just now especially interested in this field makes it desirable to give a short account of what has been done.

It was thought that by treatment of the diamide of camphoric acid with sodium hypobromite a diamine might perhaps be secured which would then yield other interesting derivatives. It was found, however, on attempting to prepare the diamide from the diethyl ester of camphoric acid by treatment with ammonia,

that even when heated with strong ammonia to 150° the ester remains almost entirely unaltered. The diamide obtained from the chloride[1] is probably unsymmetrical and its purification appears to be difficult.

Ortho-methyl Ester of Camphoraminic Acid.

The methyl ester of camphoraminic acid was next prepared, as follows: Sodium methyl camphorate was obtained by acting on camphoric anhydride with sodium methylate.[2] The dry salt was added to a little more than its weight of phosphorus oxychloride, and the mixture was added carefully to strong ammonia, taking care to keep the temperature as low as possible. The mixture of amide and imide obtained was treated with a 10-per cent. solution of sodium hydroxide, which dissolves the imide but leaves the amide unchanged. The amide was then dissolved in a small amount of strong alcohol and precipitated by the careful addition of water. When pure the amide crystallizes in white needles or prisms which melt at 152°–153°. The yield was only ten to fifteen per cent. of the weight of camphoric anhydride used, but could probably be improved by a more careful study of the conditions.

I. 0.2223 gram gave 0.5012 gram CO_2 and 0.1760 gram H_2O.
II. 0.2300 gram gave 0.5213 gram CO_2 and 0.1854 gram H_2O.
III. 0.1135 gram gave 0.00771 gram N.

	Calculated for $C_8H_{14}<^{CO_2CH_3}_{CONH_2}$.	Found. I.	II.	III.
C	61.97	61.49	61.81	...
H	8.92	8.79	8.96	...
N	6.57	...	...	6.79

Methyl Ester of Di-hydro-amino-campholytic Acid.[3]

When the amide last described is treated with a solution of sodium hypobromite it is converted into an amine, in accordance with Hoffmann's reaction.[4] 1.5 grams bromine (1 mol.) was dissolved in 32 cc. of a 5-per cent. solution of sodium hydroxide

[1] Moitessier: Ann. d. Chem. (Liebig) **120**, 253. See also Winzer: *Ibid.* **237**, 307.
[2] Walker: J. Chem. Soc. **61**, 1089.
[3] This acid is named from the relation which it bears to the campholytic acid discovered by Walker: J. Chem. Soc. **63**, 498. This is thought to be better than the introduction of another arbitrary name.
[4] Ber. d. chem. Ges. **15**, 762; **17**, 1406, 1920. See also Aschan: *Ibid.* **24**, 2715.

(4 mol.), and 2 grams of the amide (1 mol.) were added. After warming for a short time to 70°–80° the solution was cooled and extracted with ether. The amine obtained was converted into the chloride and the chloroplatinate. The *chloride* crystallizes in plates which are easily soluble in water but difficultly soluble in alcohol. It melts with decomposition at 244°. The *chloroplatinate* separates in the form of scales of a lemon-yellow color when chloroplatinic acid is added to a moderately concentrated solution of the chloride. On the spontaneous evaporation of the aqueous solution the salt was deposited in orange-colored flat needles, some of them several centimeters in length.

I. 0.0380 gram of the scales gave 0.0094 gram Pt.

II. 0.0867 gram of the scales gave 0.0218 gram Pt.

III. 0.1073 gram of the needles gave 0.0263 gram Pt.

	Calculated for $\left(C_8H_{14}<\begin{matrix}CO_2CH_3\\NH_2\end{matrix}\right)_2H_2PtCl_6$.	Found. I.	II.	III.
Pt	25.00	24.76	25.14	24.60

When the amine is heated with alcoholic soda it appears to resist saponification very strongly. After heating on the water-bath for several hours with the reagent, most of the amine was recovered, apparently unchanged. It is probable that treatment with acids would be more successful, but as a more direct method of obtaining the amino-acid has been found, and as the preparation of the amine is quite difficult, a careful study of its properties was not made. The free base separates in the form of oily drops on the addition of a solution of caustic soda to the chloride.

β-Camphoraminic Acid.

Since the structure of camphoric acid is known to be unsymmetrical, there are two possible camphoraminic acids. One of these has been recently obtained by Claissen and Manasse[1] by treating isonitroso-camphor with fuming hydrochloric acid. Apparently the same substance has been obtained by Auwers and Schnell[2] by the treatment of camphoric anhydride with strong ammonia. The camphoraminic acid described by Laurent[3] was, also, probably the same substance, but the properties are not given in sufficient detail to identify it.

[1] Ann. d. Chem. (Liebig) **274**, 81. [2] Ber. d. chem. Ges. **26**, 1522.
[3] Ann. d. Chem. (Liebig) **60**, 326.

Succinimide gives β-alanin when treated with potassium hypobromite.[1] In the hope of obtaining a similar decomposition with camphoric imide, the latter was treated with sodium hypobromite and caustic soda. While the reaction proceeds in part as desired, there was obtained also a considerable amount of a camphoraminic acid which appears to be isomeric with that referred to above. The same substance is obtained more easily by heating camphoric imide for an hour on the water-bath with a 10-per cent. solution of caustic soda. Camphoric imide dissolves in a cold solution of caustic soda and may be precipitated unchanged by carbon dioxide. After heating for an hour, however, carbon dioxide produces no precipitate in the solution. At the same time so little ammonia is evolved that a piece of litmus-paper on the lower side of a watch-glass covering the flask turns blue very slowly and no odor of ammonia is perceptible. On the addition of hydrochloric acid to the cold solution β-camphoraminic acid separates. The acid was purified by crystallization from hot water in which it is easily soluble. It crystallizes on cooling in small prisms which are difficultly soluble in cold water, but easily soluble in alcohol. From alcohol the acid is deposited in compact clear crystals belonging, apparently, to the rhombic system. These crystals are permanent in the air and do not show the slightest evidence of efflorescence. In this respect they differ from the isomer as observed by Claissen and Manasse.[2] The acid melts at 182°–183°, pure camphoric acid melting at 187° with the same thermometer. The isomer melts at 174°–176°.

I. 0.2230 gram of the acid gave 0.4921 gram CO_2 and 0.1720 gram H_2O.

II. 0.0976 gram gave 0.00716 gram N.

	Calculated for $C_8H_{14}<^{CO_2H}_{CONH_2}$.	Found. I.	II.
C	60.30	60.18	...
H	8.54	8.57	...
N	7.04	...	7.34

Di-hydro-amino-campholytic Acid.

After the action of caustic soda on camphoric imide had been discovered, the following method of converting it into di-hydro-amino-campholytic acid was used: 3.6 grams of the imide

[1] Hoogewerff and v. Dorp, R. 10, 5. [2] *Loc. cit.*

(1 molecule) were dissolved in 48 cc. of 10-per cent. caustic soda (6 molecules), and the solution was heated for three-fourths of an hour on the water-bath. The solution was then cooled and 3.2 grams (1 molecule) of bromine was added. The solution was then warmed again for ten minutes on the water-bath. After cooling, a little sodium sulphite was added, and then hydrochloric acid of known strength in sufficient amount to combine with the sodium not combined with the bromine. The solution was then evaporated nearly to dryness, and enough more hydrochloric acid to combine with the amino-acid was added. The residue was then extracted with strong alcohol, leaving most of the sodium chloride undissolved. The alcoholic solution was then evaporated at a gentle heat, and the residue was neutralized with a 10-per cent. solution of caustic soda until a drop of the solution reacted faintly alkaline with phenol phthaleïn. This causes the separation of a considerable portion of the amino-acid. The acid may be purified by crystallization from water, but for analysis was purified by dissolving in water and adding two or three volumes of acetone. If the amount of acetone added is small, the substance separates in small granular crystals; if more is used, and especially if added quickly, it forms white pearly scales. When heated on platinum foil or in a small tube the acid sublimes without melting and with almost no decomposition. It is almost insoluble in alcohol, acetone or ether. It dissolves easily in water, but is scarcely more soluble in hot than in cold water. The aqueous solution is neutral toward litmus. The *chloride* is easily soluble in alcohol and in water. The *chloroplatinate* is also easily soluble in water.

I. 0.1103 gram of the granular crystals gave 0.2568 gram CO_2 and 0.0978 gram H_2O.

II. 0.1157 gram of the scales gave 0.0968 gram N.

	Calculated for $C_8H_{14}{<}^{CO_2H}_{NH_2}$.	Found. I.	Found. II.
C	63.16	63.50	...
H	9.94	9.89	...
N	8.13	...	8.37

It is hoped that by the action of nitrous acid the body may be converted into the corresponding hydroxy acid. It may be, too, that a second dihydro amino-campholytic-acid can be obtained from the camphoraminic acid of Claissen and Manasse. The work will be continued in these directions.

TERRE HAUTE, *March* 1, 1894.

REVIEW.

LECTURE-NOTES ON THEORETICAL CHEMISTRY. By FERDINAND G. WIECHMANN, Ph. D., Instructor in Chemical Physics and Chemical Philosophy, School of Mines, Columbia College. 226 pp. + xiv, 8vo. New York: Wiley, 1893.

This book is intended for students in the earlier stages of their course in chemistry. The author remarks: "It has been the intention of the writer to offer a general view over the wide domain of chemical theory, to exhibit, as clearly as might be, the correlation of the many lines of research along which investigations of the questions of theoretical chemistry are at present conducted, and, last but not least, to point out the practical bearing of its teachings on problems to be constantly met with in the application of chemical knowledge."

A good deal of information has been brought together in systematic form, and due attention has been paid to the new problems that are now under investigation. Thus, a few pages are devoted to stereochemistry, and to the new methods of determining molecular weights by observations on the osmotic pressure, the elevation of the boiling-point, and the depression of the freezing-point of solutions. The limits of the book prevent anything like a full discussion of the subjects treated. Some are, however, treated more fully than seems necessary, while others are not clearly presented, because too briefly. For example, the statements in regard to osmotic pressure on pages 73 and 74 do not give any conception in regard to this kind of pressure; while under the head of molecular refraction, pages 81 and 82, the refraction of light is explained in some detail. This is not very serious, but the book could be improved by better balancing.

Taken all in all the treatise of Dr. Wiechmann presents the subject of theoretical chemistry intelligently and clearly. I. R.